Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Visible-light-mediated, simple copper(I)-chloride catalysed efficient C_{sp}-C_{sp} homocoupling of terminal alkynes at room temperature

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Experimental section

General: All reactions were conducted under an oxygen atmosphere and oven-dried glass wares were used. All reactions were conducted using a blue light-emitting diode (LED) as the visible-light source (30 lamps, power density: 40 mW/cm^2 at 460 nm). All solvents were dried according to known methods and distilled prior to use. Starting materials (including starting materials for synthesis of epoxide hydrolase inhibitors) were commercially available (Sigma-Aldrich or Alfa-Aesar or TCI-chemicals) and used as received. NMR spectra were recorded ^{1}H NMR at 400 MHz/ ^{13}C NMR at 100 MHz using deuterated $CDCl_3$. Chemical shifts (δ) were reported as parts per million (ppm) and the following abbreviations were used to identify the multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet, b= broad and all combinations thereof can be explained by their integral parts. Unless otherwise specified, the proton/carbon signal of 2 residual solvent (at δ 7.24 and δ 77.00 ppm, respectively) was used as the internal reference.

General procedure:

A dry test tube (20 mL) with rubber septum and magnetic stirrer bar was charged with terminal alkynes (1mmol) and 5 mol% CuCl in CH_3CN (1 mL). The mixture was fixed with blue LEDs (the temperature reaches between 25-30 ^oC when doing irradiation in blue-LEDs) under oxygen atmosphere and continued for the irradiation until completion of homocoupling reaction (it was determined by thin layer chromatography). The reaction mixture was diluted with 40 % ethyl acetate in hexane and stirred in for 10 min. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel (using n-hexane and ethyl acetate as eluent) to afford desired homocoupling product. The ratio of n-hexane and ethyl acetate varies depending on the polarity of the terminal alkynes used for the formation of homocoupling product. For example, product **(2a)** 1,4-diphenylbuta-1,3-diyne is a non-polar and can be eluted out by using only n-hexane, whereas product like **(2q)** 3,3'-(buta-1,3-diyne-1,4-diyl) dibenzonitrile is quite polar and could be eluted out by using n-hexane and ethyl acetate in the ratio 10:1.

Procedure for the preparation of Phenylacetylene-d_1: [s1]

A dry round bottom flask (100 mL) with rubber septum and magnetic stirrer bar was charged with phenyl acetylene (1g) and THF (5-7 mL) and then reaction mixture temperature was the lower down to -78 ^oC by using ethanol and liquid nitrogen. To this above mixture, n-butyllithium solution (15% hexane) (1.5 eqv.) was added and reaction temperature was maintained -78 ^oC for 45 min. and then when reaction temperature was about 10-15 ^oC at that time D_2O was added and reaction was continued for 4 h. Product was separated by layer separation using ethyl ether. Product was characterized by ^1H, ^{13}C NMR[S2] and HR-MS.

Evaluation of Green metrics of the process;

Atom economy defined as "how much of the reactants remain in the final desired product"

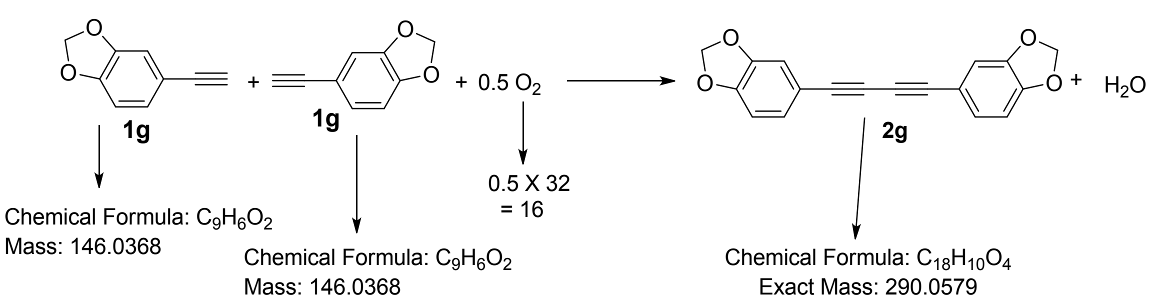
$$\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

Reaction mass efficiency (RME) defined as "the percentage of the mass of the reactants that remain in the product"

$$\text{Reaction mass efficiency (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100$$

a) Scheme S1: Evaluation of Green metrics of the current photochemical process

Reaction scheme



Total= 146+146+16 = 308

Reactant	5-ethynylbenzo[d][1,3]dioxole (**1g**)	1.022g	0.007mol	FW 146.03
Solvent	ACN	10g	---	---
Auxiliary	---	---	---	---
Product	1,4-bis(benzo[d][1,3]dioxol-5-yl)buta-1,3-diyne (**2g**)	1.78g	0.006mol	FW 290.05

Product yield= 88%

$$\text{E-factor} = \frac{1.022\text{g} + 1.022\text{g} + 10.0\text{ g} - 1.78\text{g}}{1.78\text{ g}} = 5.76\text{kg waste/ 1 kg product}$$

$$\text{Atom economy} = \frac{290}{308} \times 100 = 94\%$$

$$\text{Atom efficiency} = 88\% \times 94\% / 100 = 82\%$$

$$\text{Carbon efficiency} = \frac{18}{9+9} \times 100 = 100\%$$

$$\text{Reaction mass efficiency} = \frac{1.78\text{ g}}{1.022\text{g} + 1.022\text{g}} \times 100 = 87\%$$

Calculation of TOF (our process):

Reaction condition: 5 mol% CuCl, CH_3CN solvent at room temperature **(**in a gram scale**)**

Product yield= 88%

TON= moles of terminal alkynes (**1g**)/moles of CuCl-catalyst

= 0.007 moles/0.00035

= **20**

Actual TON= 20 x 0.88 = **17.6**

TOF= 17.6 turnover/10 h (time)

= **1.76 h^{-1}**

Reaction condition: 5 mol% CuCl, CH_3CN solvent at room temperature

Product yield= 98%

TON= moles of terminal alkynes /moles of CuCl-catalyst

= 1 mole/0.05

= **20**

Actual TON= 20 X 0.98 = **19.6**

TOF= 19.6 turnover/7h (time)

= **2.8 h^{-1}**

Calculation of TOF (reported thermal process):[S3]

Reaction condition: 5 mol% CuCl, DMSO solvent at 90 ^{o}C

Product yield= **96%**

TON= moles of terminal alkynes (**1g**)/moles of CuCl-catalyst

= 0.001 moles/0.00005

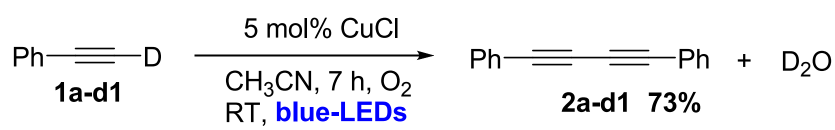
= **20**

Actual TON= 20 X 0.96 = **19.2**

TOF= 19.2 turnover/7 h (time)

= **2.74 h^{-1}**

Scheme S2: Isotope labeling experiment



the experiment with phenylacetylene-d$_1$ as starting material instead of phenylacetylene (**1a**), this result furnished the homocoupling product (1,3-diynes) in 73% yield after 7 h irradiation under standard condition (see in table 1, entry 18). Also, the experiment with phenylacetylene and phenylacetylene-d$_1$**,** where the reaction mixture was irradiated only for 4 h. These reactions of phenylacetylene-H and phenylacetylene-d$_1$ resulted in 81% and 66% yields, respectively. Based on these above results, the kinetic isotopic effect (KIE= K_H/K_D) was found to be [81/66 + 98/73]/2= 1.3.

Table S1

Entry	Reaction time (hr)	%Yield Phenylacetylene	%Yield Phenylacetylene-D1
1.	4	81	66
2.	7	98	73

EPR spectra of the reaction mixture after blue LEDs irradiation

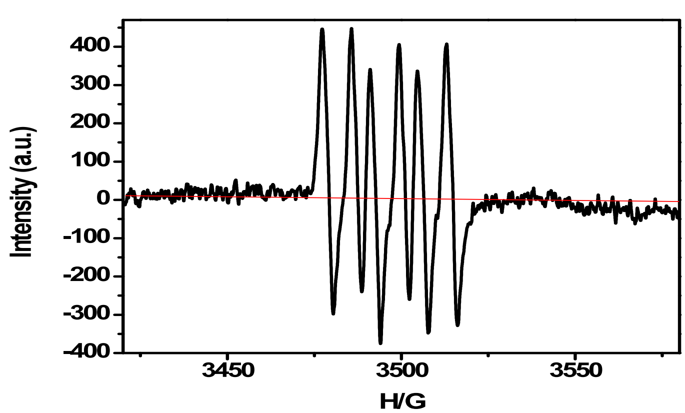


Figure S1. EPR spectra of the reaction mixture: phenylacetylene(**1a**) (0.6 M), and 5 mol% of CuCl in CH_3CN, 0.5 mL of this reaction solution was taken out into a small vial, followed by the addition of 0.01 ml of DMPO (5×10^{-2} M). The mixture was irradiated with blue LEDs at room temperature under an oxygen atmosphere (1 atm) for 30 minutes. The reaction mixture was then analysed by EPR spectra. There are classical 6 peaks, the signals corresponding to (DMPO-OO(H)).

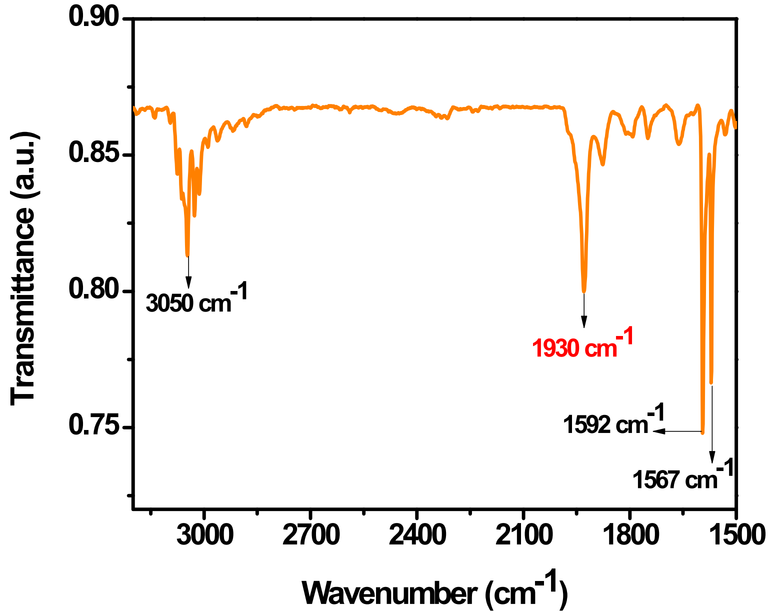


Figure S2. FT-IR-spectra of in-situ generated copper(I) phenylacetylide. IR (KBr, cm^{-1}): 3050 (aromatic C-H stretching), 1930 (C≡C-Cu^{I}), 1596 and 1568 (aromatic C=C stretching).

References:

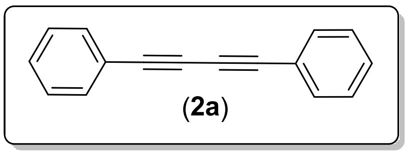
S1: J.J Eisch, Wei Liu, L.Zhu, A.L. Rheingold*, Eur. J. Org. Chem.* 2015, 7384.

S2: *Chem. Commun*., 2016, 52, 4509--4512

S3: K. Yin, C. Li, J. Li, X. Jia, *Green Chem.,* 2011, **13**, 591

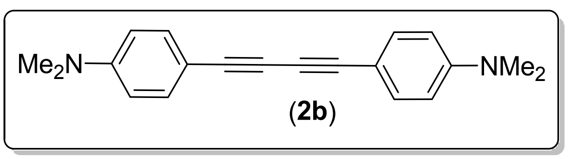
Spectroscopic Data:

1, 4-diphenylbuta-1,3-diyne (2a)



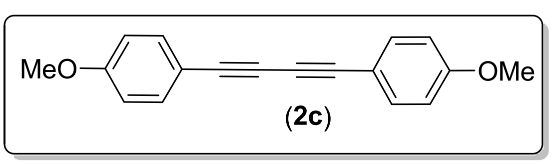
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 4 H), 7.36-7.30 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.4, 129.1, 128.4, 121.7, 81.5 and 73.8; **HRMS** calcd for $C_{16}H_{10}$: 202.078, found: 202.075.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(N,N-dimethylaniline) (2b)



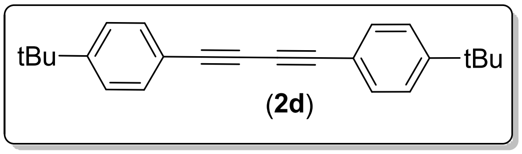
Pale orange solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J*= 8.0 Hz, 4 H), 6.59 (d, *J*= 8.0 Hz, 4 H), 2.96 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.3, 133.6, 111.6, 108.6, 82.3, 72.6 and 40.1; **HRMS** calcd for $C_{20}H_{20}N_2$: 288.163, found: 288.162.

1,4-bis(4-methoxyphenyl)buta-1,3-diyne (2c)



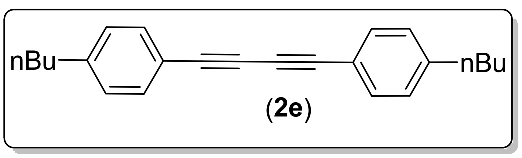
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J*= 8.0 Hz, 4 H), 6.83 (d, *J*= 8.0 Hz, 4 H), 3.80 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.2, 134.0, 114.1, 113.9, 81.2, 72.9, 55.3 and 29.6; **HRMS** calcd for $C_{18}H_{14}O_2$: 262.099, found: 262.099.

1,4-bis(4-(tert-butyl)phenyl)buta-1,3-diyne (2d)



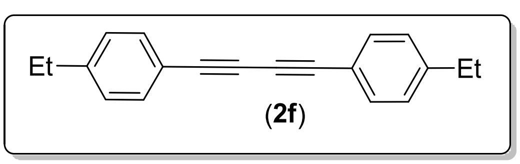
White solid; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J*=8.0 Hz, 4 H), 7.33 (d, *J*=8.0 Hz, 4 H), 1.29 (s, 18 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 152.5, 132.2, 125.4, 118.8, 81.4, 73.4, 34.8 and 31.0; **HRMS** calcd for $C_{24}H_{26:}$ 314.203, found: 314.202.

1,4-bis(4-butylphenyl)buta-1,3-diyne (2e)



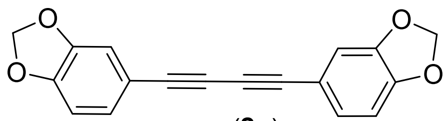
White solid; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, *J*=4.0 Hz, 4 H), 7.13 (d, *J*=4.0 Hz, 4 H), 2.6 (t, *J*=4.0 Hz, 4 H), 1.60-1.54 (m, 4 H), 1.35-1.32 (m, 4 H), 0.91 (t, *J*=4.0 Hz, 6 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 144.4, 132.3, 128.5, 118.9, 81.5, 73.4, 35.6, 33.2, 22.2 and 13.8; **HRMS** calcd for $C_{24}H_{26}$: 314.2035, found: 314.2031

1,4-bis(4-ethylphenyl)buta-1,3-diyne (2f)



Yellow solid; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, *J*=8.0 Hz, 4 H), 7.16 (d, *J*=8.0 Hz, 4 H), 2.65 (q, *J*=8.0 Hz, 4 H) 1.23 (t, *J*=8.0 Hz, 6 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 145.7, 132.4, 127.9, 118.9, 81.5, 73.4, 28.8 and 15.2; **HRMS** calcd for $C_{20}H_{18:}$ 258.141, found: 258.140.

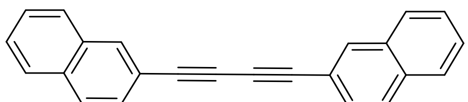
1,4-bis(benzo[d][1,3]dioxol-5-yl)buta-1,3-diyne (2g)



(**2g**)

White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.04 (d, *J*=8.0 Hz, 2 H), 6.91 (s, 2 H), 6.74 (d, *J*=8.0 Hz, 2 H), 5.97 (s, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.7, 147.4, 127.6, 114.9, 112.0, 108.6, 101.4, 81.2, and 72.5; **HRMS** calcd for $C_{18}H_{10}O_4$: 290.0579 found: 290.0581

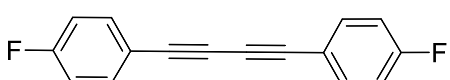
1,4-di(naphthalen-2-yl)buta-1,3-diyne (2h)



(**2h**)

Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (s, 2 H), 7.82-7.78 (m, 6 H), 7.56-7.49 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 133.1, 133.0, 132.8, 128.4, 128.1, 127.8, 127.2, 126.7, 119.0, 82.2, 74.3 and 29.6; **HRMS** calcd $C_{24}H_{14}$: 302.110, found: 302.109.

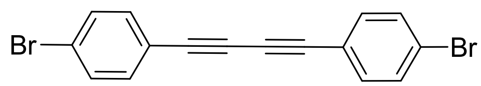
1,4-bis(4-fluorophenyl)buta-1,3-diyne (2i)



(**2i**)

Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.47 (m, 4 H), 7.03-6.99 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.3, 161.8, 134.5, 134.4, 116.0, 115.7, 80.4 and 73.5; **HRMS** calcd for $C_{16}H_8F_2$: 238.059, found: 238.059.

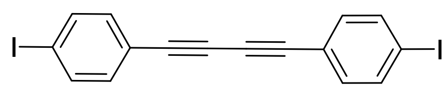
1,4-bis(4-bromophenyl)buta-1,3-diyne (2j)



(**2j**)

White Solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, *J*=4.0 Hz, 4 H), 7.36 (d, *J*=4.0 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 133.8, 131.8, 123.9, 120.7, 81.0 and 74.9; **HRMS** calcd for $C_{16}H_8Br_2$: 357.899, found: 357.900.

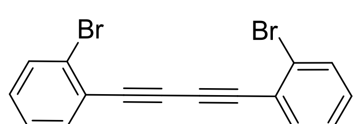
1,4-bis(4-iodophenyl)buta-1,3-diyne (2k)



(**2k**)

White Solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J*=4.0 Hz, 4 H), 7.22 (d, *J*=4.0 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.7, 133.8, 121.28, 94.3, 81.3 and 75.2; **HRMS** calcd for $C_{16}H_8I_2$: 453.8715, found: 453.8710.

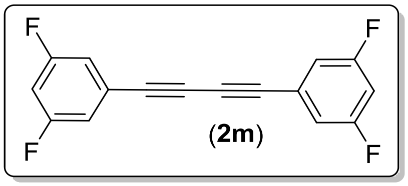
1,4-bis(2-bromophenyl)buta-1,3-diyne (2l)



(**2l**)

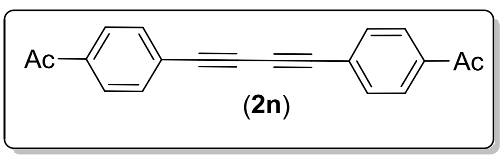
Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 2 H), 7.29-7.18 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.5, 132.5, 130.3, 127.0, 126.1, 124.0, 81.0 and 76.6; **HRMS** calcd for $C_{16}H_8Br_2$: 357.899, found: 357.900.

1,4-bis(3,5-difluorophenyl)buta-1,3-diyne (2m)



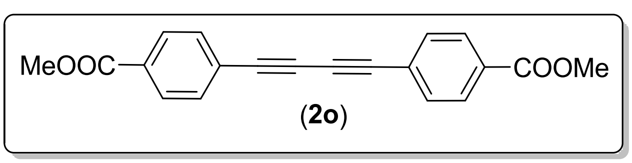
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.04-7.01 (m, 2 H), 6.87-6.82 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.9, 163.8, 161.5, 161.3, 124.0, 123.9, 123.8, 115.6, 115.4, 106.2, 106.0, 105.7, 80.0 and 75.0; **HRMS** calcd for $C_{16}H_6F_4$: 274.041, found: 274.040.

1,1'-(buta-1,3-diyne-1,4-diylbis(4,1-phenylene))diethanone (2n)



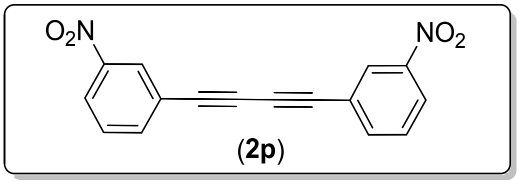
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.89 (d, *J*= 8.0 Hz, 4 H), 7.59-7.57 (d, *J*= 8.0 Hz, 4 H), 2.57 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.0, 137.0, 132.6, 128.2, 126.1, 81.9, 76.4 and 26.6; **HRMS** calcd for $C_{20}H_{14}O_2$: 286.099, found: 286.098.

Dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate (2o)



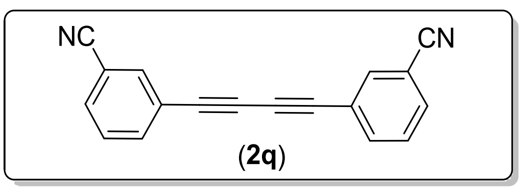
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.00-7.98 (m, 4 H), 7.58-7.56 (m, 4 H), 3.99 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.2, 132.4, 130.4, 129.5, 126.0, 81.8, 76.2 and 52.3; **HRMS** calcd for $C_{20}H_{14}O_4$: 318.089, found: 318.089.

1,4-bis(3-nitrophenyl)buta-1,3-diyne (2p)



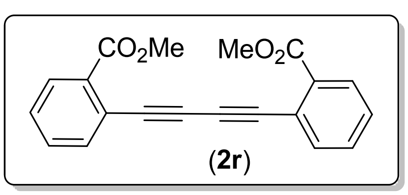
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (t, *J*=0.8 Hz, 2 H), 8.26-8.23 (m, 2 H), 7.85-7.82 (m, 2 H) 7.58-7.54 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.0, 138.0, 129.6, 127.3, 124.1, 123.0, 79.9 and 75.4; **HRMS** calcd for $C_{16}H_8N_2O_4$: 292.048, found: 292.048.

3,3'-(buta-1,3-diyne-1,4-diyl)dibenzonitrile (2q)



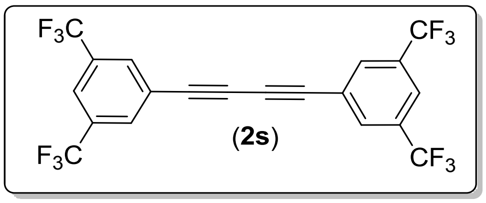
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78-7.70 (m, 2 H), 7.66 (d, *J*=4.0 Hz, 2 H), 7.64 (d, *J*=4.0 Hz, 2 H), 7.48-7.45 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.4, 135.7, 132.6, 129.5, 123.0, 117.6, 113.2, 79.9 and 75.4; **HRMS** calcd for $C_{18}H_8N_2$: 252.0687, found: 252.0684.

Dimethyl 2,2'-(buta-1,3-diyne-1,4-diyl)dibenzoate (2r)



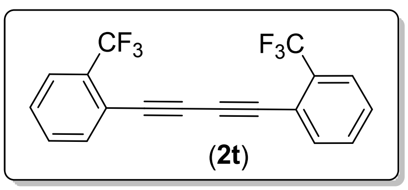
Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, *J*=4.4 Hz, 2 H), 7.65 (d, *J*=4 Hz, 2 H), 7.49-7.38 (m, 4 H), 3.94 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.1, 135.1, 132.7, 131.8, 130.59, 128.7, 122.5, 81.4, 76.7 and 52.3; **HRMS** calcd for $C_{20}H_{14}O_4$: 318.0892, found: 318.0890.

1,4-bis(3,5-bis(trifluoromethyl)phenyl)buta-1,3-diyne (2s)



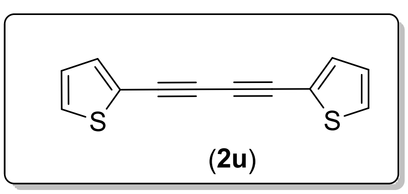
Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (s, 4 H), 7.87 (s, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.8, 132.5, 132.4, 132.1, 131.8, 126.7, 124.0, 123.5, 123.0, 121.3, 118.6, 79.6 and 76.0; **HRMS** calcd for $C_{20}H_6F_{12}$: 474.028, found: 474.024.

1,4-bis(2-(trifluoromethyl)phenyl)buta-1,3-diyne (2t)



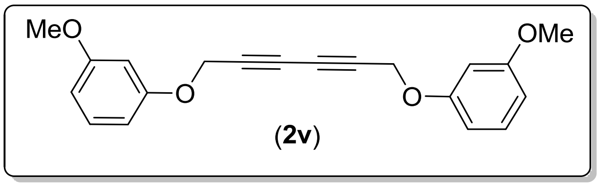
Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (t, *J*=4.0 Hz, 4 H), 7.53-7.44 (m, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.1, 131.5, 129.1, 126.09, 126.04, 125.99, 125.94, 125.5, 119.6, 78.6 and 76.68; **HRMS** calcd for $C_{18}H_8F_6$: 338.053, found: 338.050.

1,4-di(thiophen-2-yl)buta-1,3-diyne (2u)



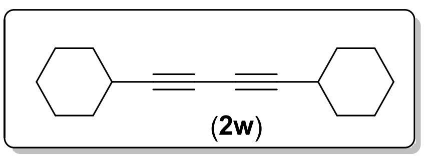
Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.30 (m, 4 H), 6.99-6.97 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.3, 128.9, 127.2, 121.9, 77.7 and 76.6; **HRMS** calcd for $C_{12}H_6S_2$: 213.9911, found: 213.9908.

1,6-bis(3-methoxyphenoxy)hexa-2,4-diyne (2v)



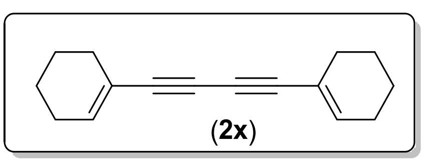
Pale white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18 (t, *J*=8.0 Hz, 2 H), 6.56-6.48 (m, 6 H), 4.71 (s, 4H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.7, 158.5, 129.9, 107.3, 106.7, 101.4, 73.3, 71.0, 56.1 and 55.2; **HRMS** calcd for $C_{20}H_{18}O_4$: 322.1205, found: 322.1202.

1,4-dicyclohexylbuta-1,3-diyne (2w)



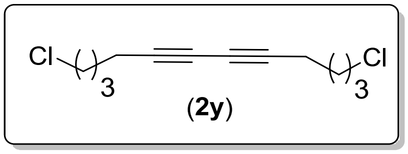
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.43-2.38 (m, 2 H), 1.95-1.76 (m, 7 H), 1.74-1.65 (m, 7 H), 1.56-1.40 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 81.8, 65.0, 39.7, 32.2, 25.7 and 24.7; **HRMS** calcd for $C_{16}H_{22}$:214.1722, found: 214.1725.

1,4-di(cyclohex-1-en-1-yl)buta-1,3-diyne (2x)



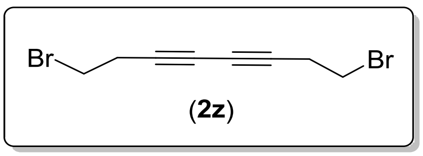
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.22-6.20 (m, 2 H), 2.10-2.07 (m, 8 H), 1.60-1.56 (m, 8 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.0, 119.9, 82.6, 71.5, 28.6, 25.8, 22.0 and 21.2; **HRMS** calcd for $C_{16}H_{18:}$ 210.1409, found: 210.1406.

1,8-dichloroocta-3,5-diyne (2y)



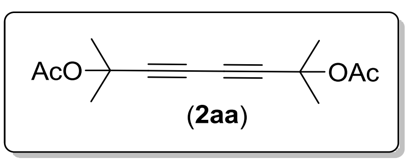
Pale yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 3.52 (t, *J*=8.0 Hz, 4 H), 2.27 (t, *J*=8.0 Hz, 4 H), 1.86 (q, *J*=8.0 Hz, 4 H), 1.64 (q, *J*=8.0 Hz, 4 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 65.7, 44.3, 31.3, 25.4 and18.4; **HRMS** calcd for $C_{12}H_{16}Cl_2$: 230.063, found: 230.062.

1,8-dibromoocta-3,5-diyne (2z)



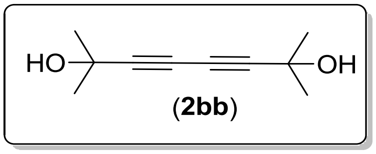
White solid; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 3.40 (t, *J*=8 Hz, 4 H), 2.81 (t, *J*=8 Hz, 4 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 74.9, 66.8, 28.4 and 23.66; **HRMS** calcd for $C_8H_8Br_2$: 216.8993, found: 216.8990.

2,7-dimethylocta-3,5-diyne-2,7-diyl diacetate (2aa)



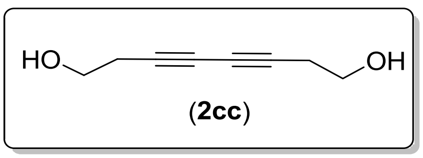
Pale yellow solid; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 1.96 (s, 6 H), 1.59(s, 12 H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 169.1, 80.3, 71.6, 68.3, 28.5 and 21.6; **HRMS** calcd for $C_{14}H_{18}O_4$: 250.121, found: 250.119.

.2,7-dimethylocta-3,5-diyne-2,7-diol (2bb)



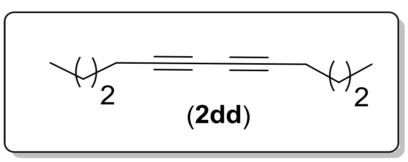
Pale yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.03 (s, OH), 1.50 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 89.9, 66.3, 65.5 and 31.0; **HRMS** calcd for $C_{10}H_{14}O_2$: 166.099, found: 166.098.

Octa-3,5-diyne-1,8-diol (2cc)

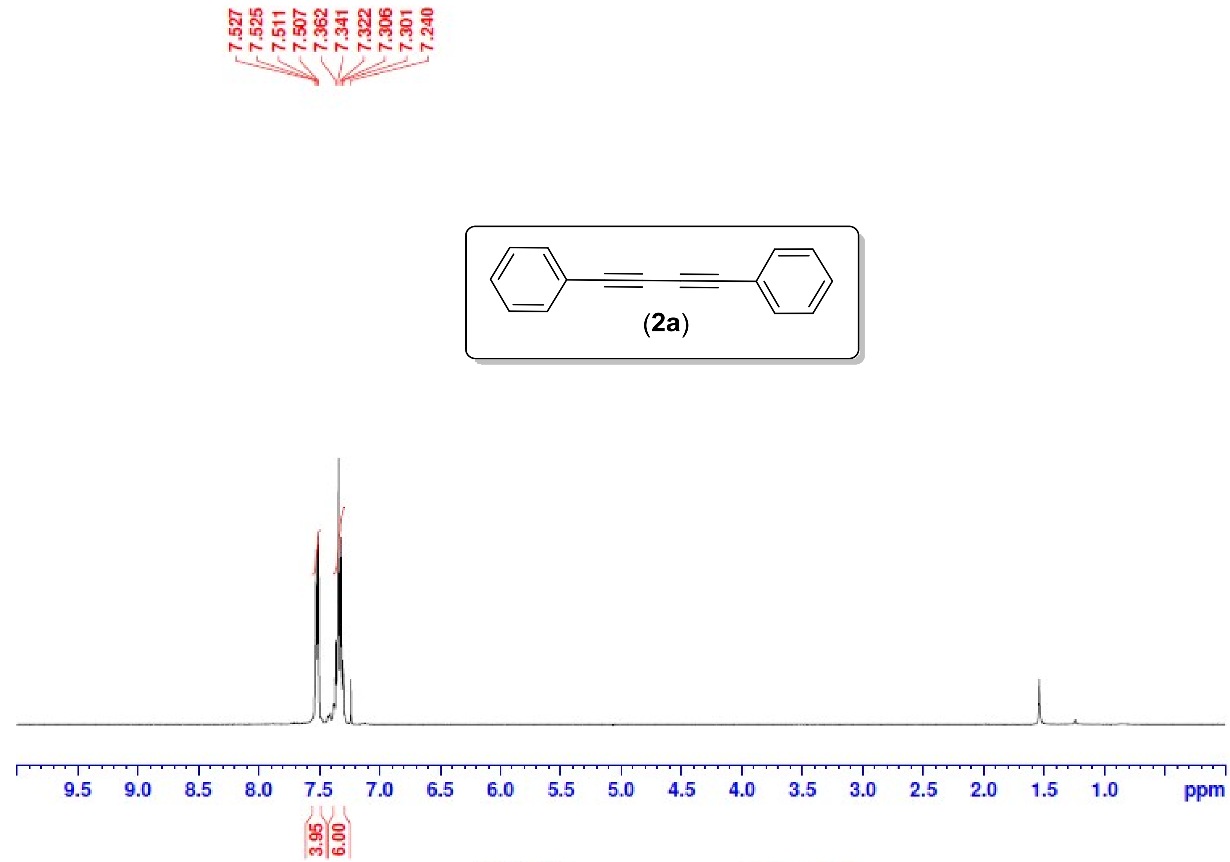


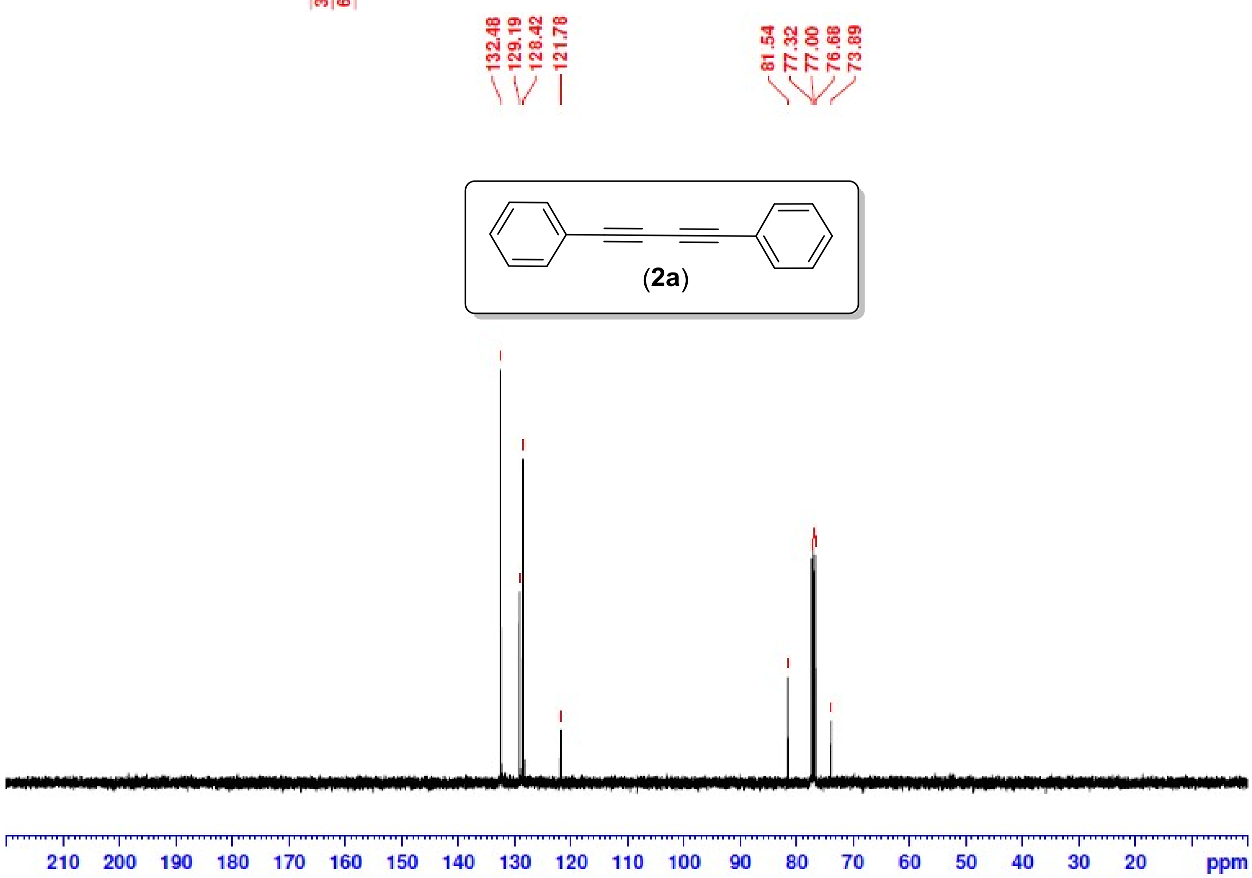
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.69 (t, J=4 Hz, 4 H), 2.80 (s, OH), 2.49 (t, J=4 Hz, 4 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 74.7, 66.5, 60.6 and 23.4; **HRMS** calcd for $C_8H_{10}O_2$: 138.0681, found: 138.0683.

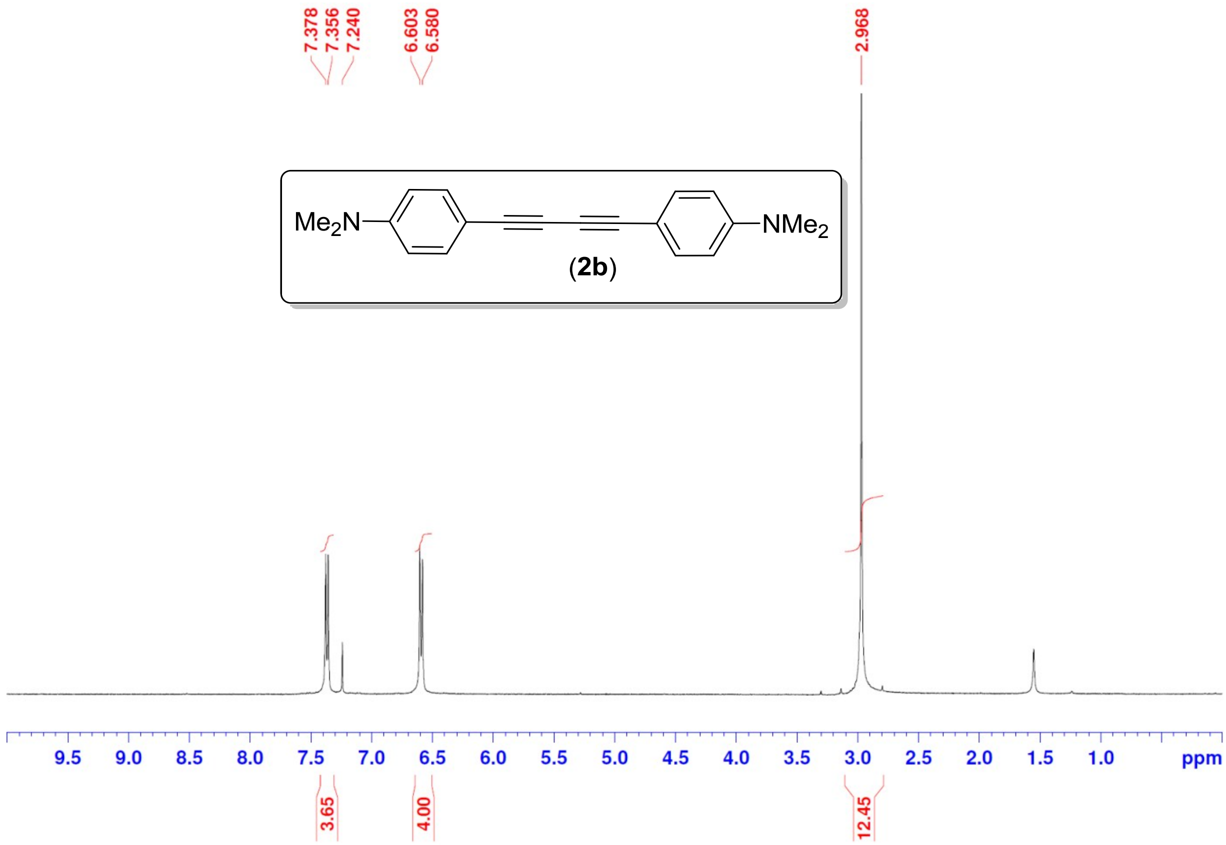
Dodeca-5,7-diyne (2dd)

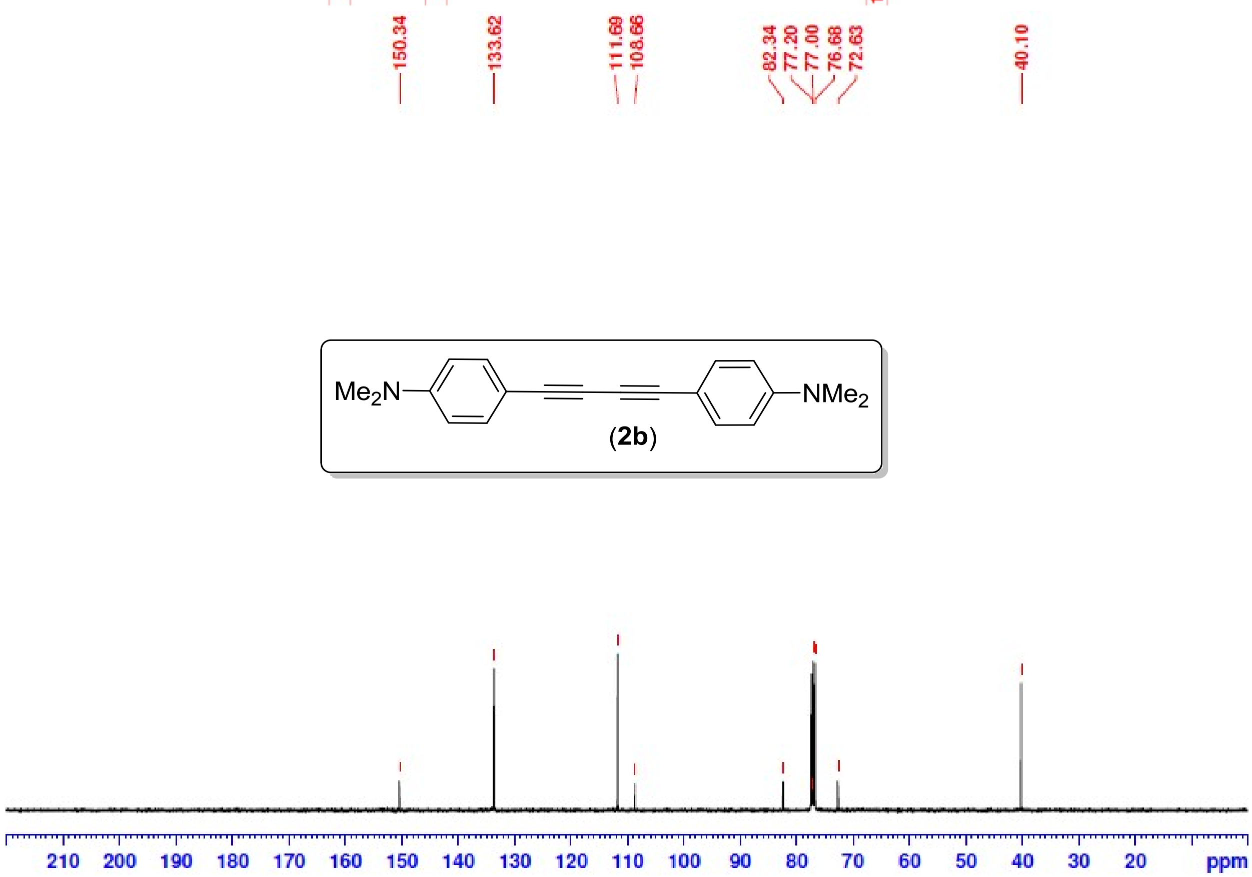


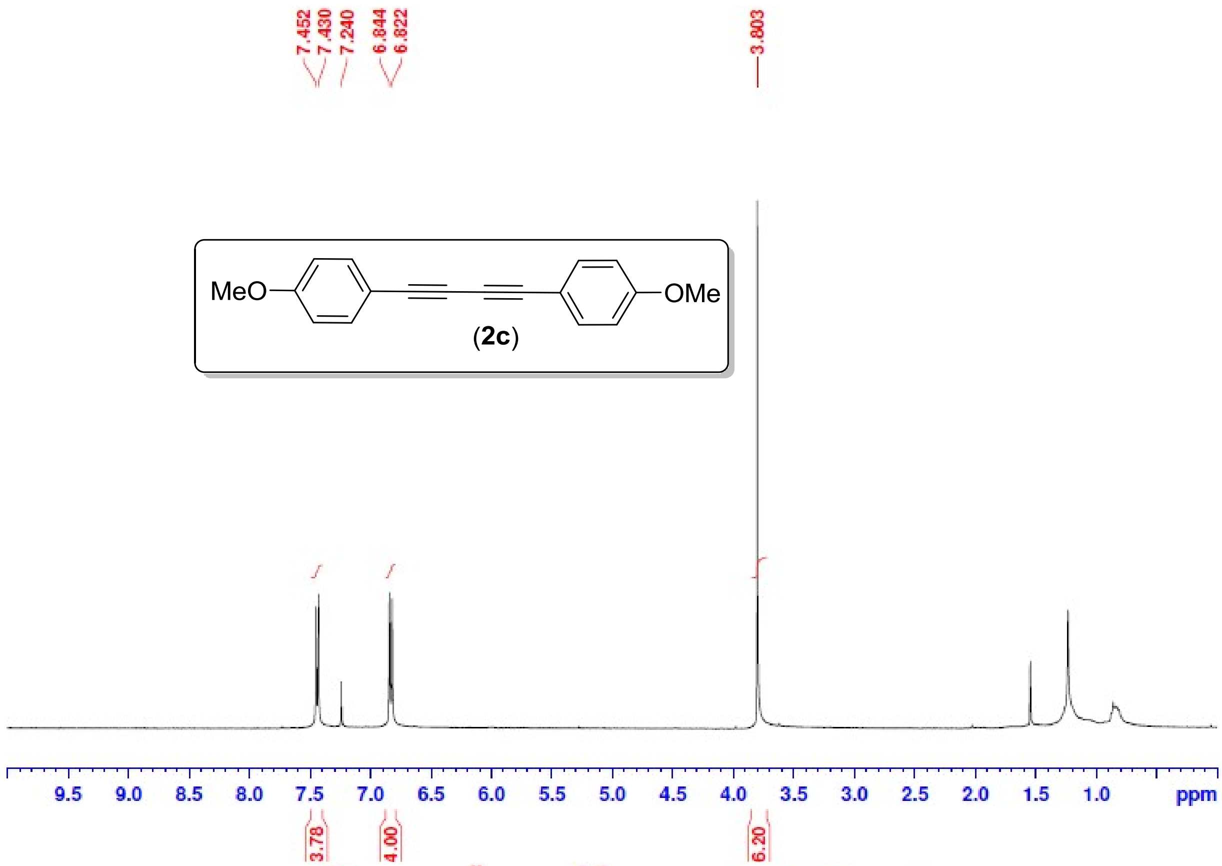
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.21 (t, *J*=8.0 Hz, 4 H), 1.49-1.32 (m, 8 H), 0.86 (t, *J*=8.0 Hz, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 77.3, 65.2, 30.3, 21.8, 18.8 and 13.4; **HRMS** calcd for $C_{12}H_{18}$: 162.1409, found: 162.1408.

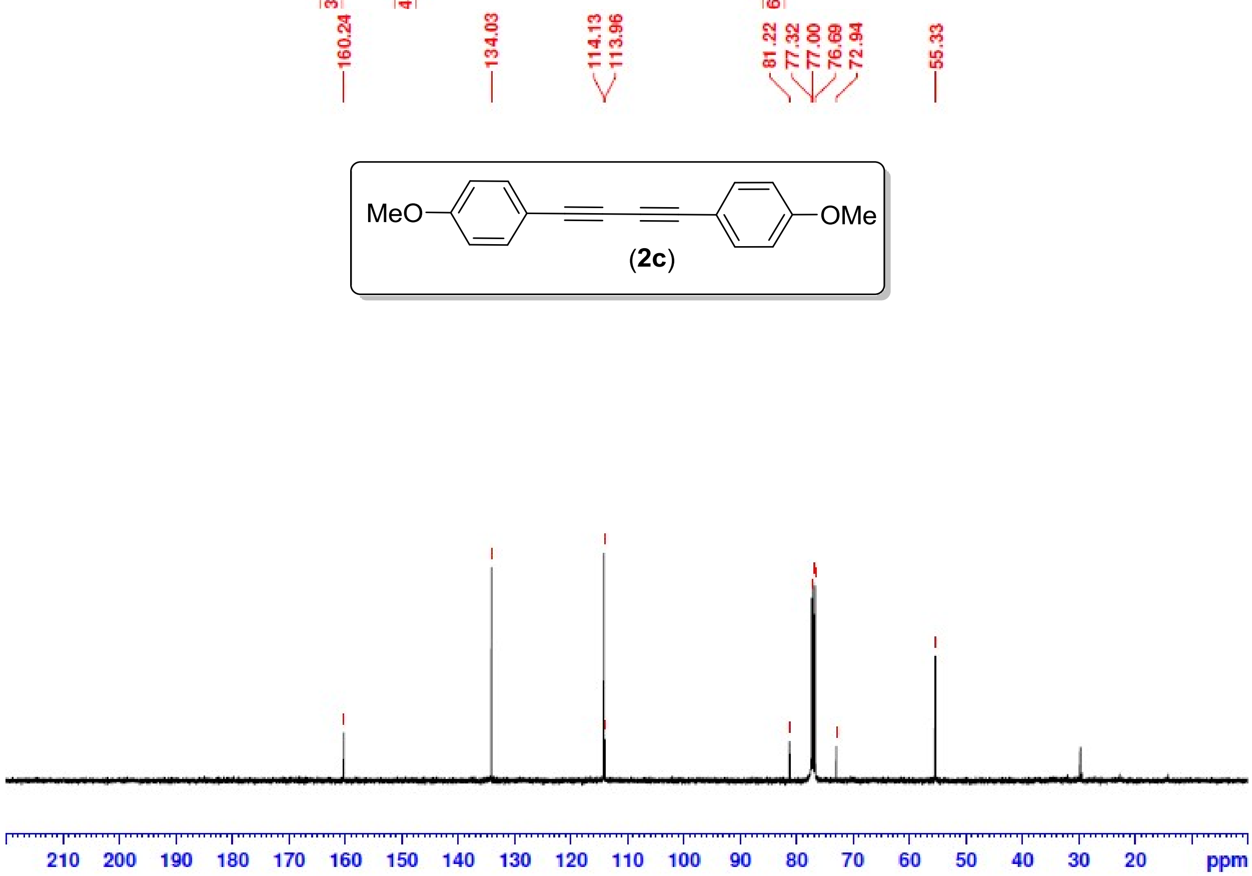

7.527
7.525
7.511
7.507
7.362
7.341
7.322
7.306
7.301
7.240
(2a)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.95
6.00

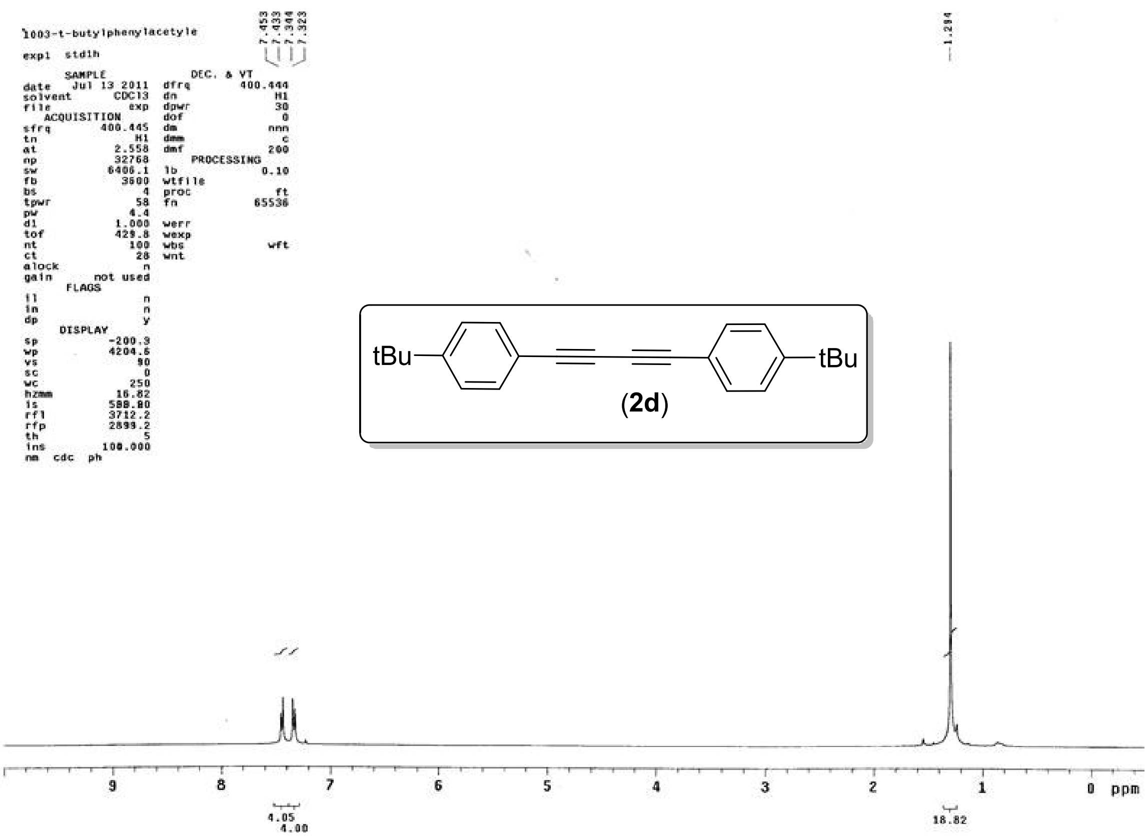

132.48
129.19
128.42
121.78
81.54
77.32
77.00
76.68
73.89
(2a)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

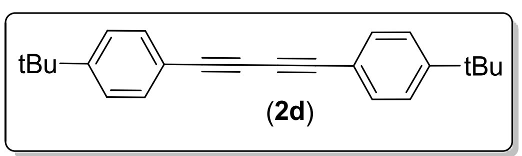

7.378
7.356
7.240
6.603
6.580
2.968
Me2N
NMe2
(2b)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.65
4.00
12.45


150.34
133.62
111.69
108.66
82.34
77.20
77.00
76.68
72.63
40.10
Me2N
NMe2
(2b)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

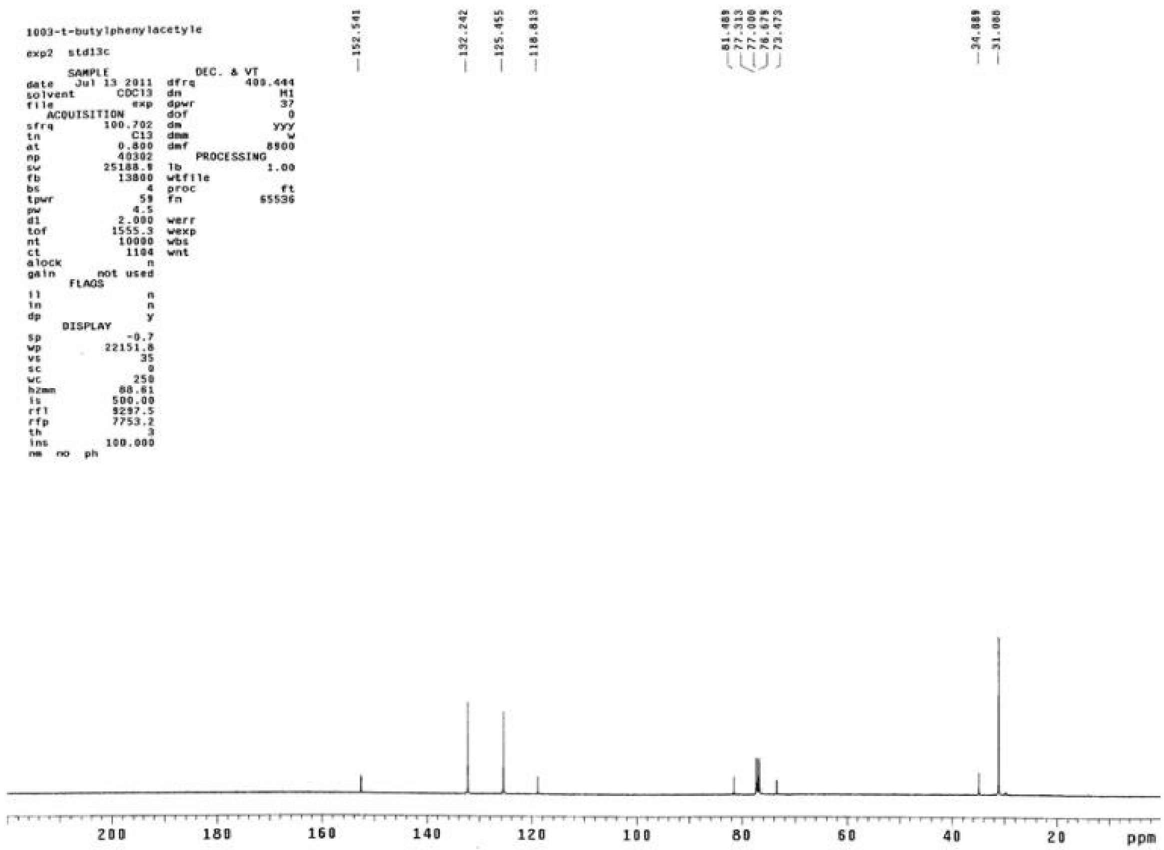

7.452
7.430
7.240
6.844
6.822
3.803
MeO
OMe
(2c)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.78
4.00
6.20

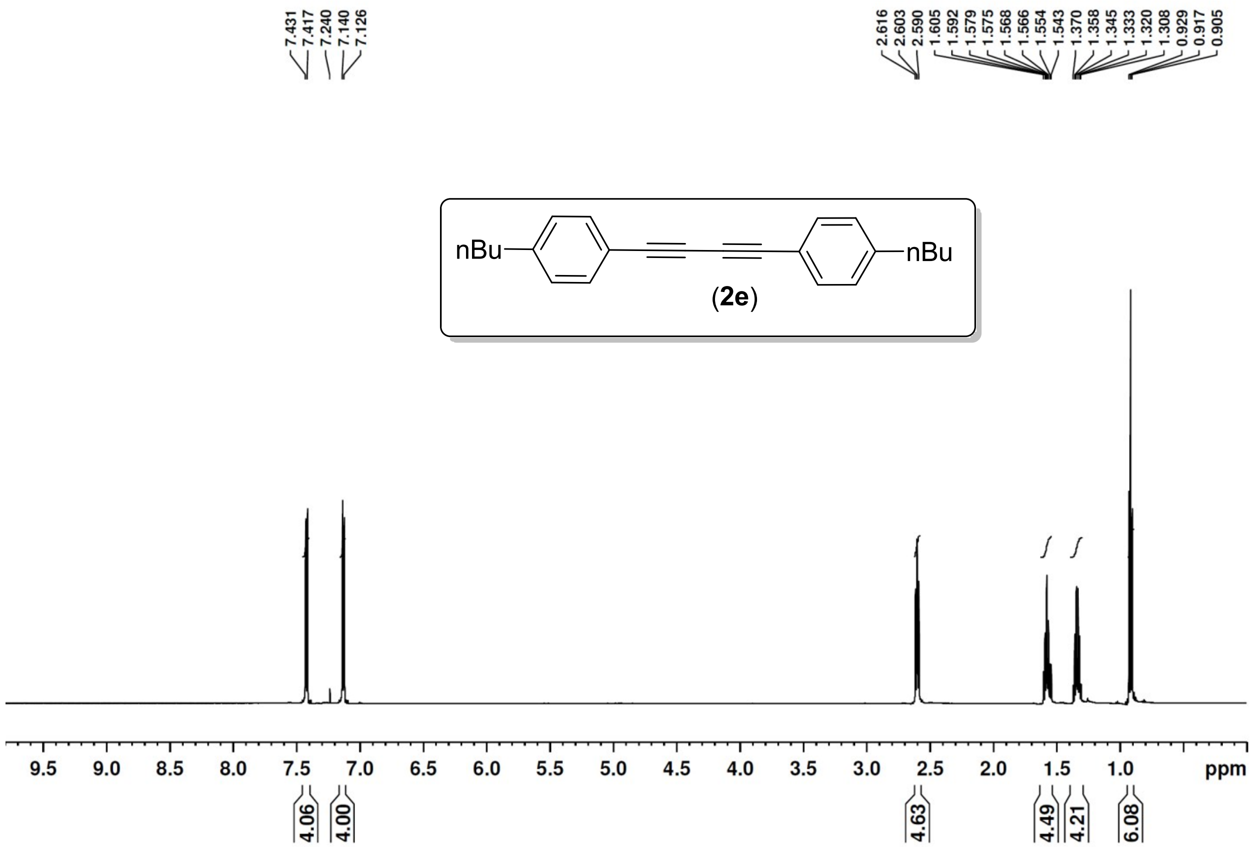

160.24
134.03
114.13
113.96
81.22
77.32
77.00
76.69
72.94
55.33
MeO
OMe
(2c)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

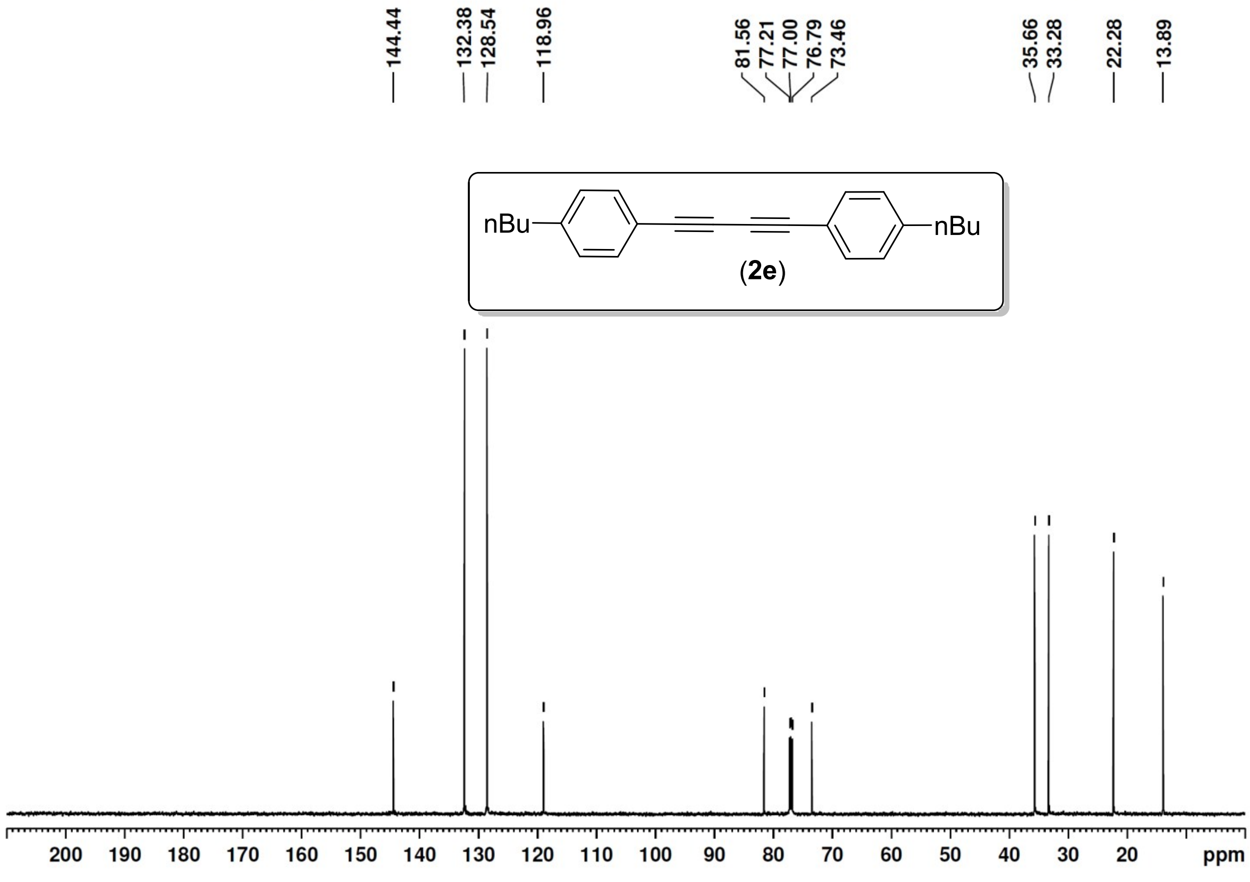

1003-t-butylphenylacetyle
exp1 std1h
SAMPLE
date Jul 13 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 400.445
tn H1
at 2.558
np 32768
sw 6406.1
fb 3600
bs 4
tpwr 58
pw 4.4
d1 1.000
tof 429.8
nt 100
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -200.3
wp 4204.6
vs 90
sc 0
wc 250
hzmm 16.82
is 588.80
rfl 3712.2
rfp 2899.2
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.444
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
lb 0.10
wtfile
proc ft
fn 65536
werr
wexp
wbs wft
wnt
7.453
7.433
7.344
7.323
1.294
tBu
tBu
(2d)
9
8
7
6
5
4
3
2
1
0 ppm
4.05
4.00
18.82

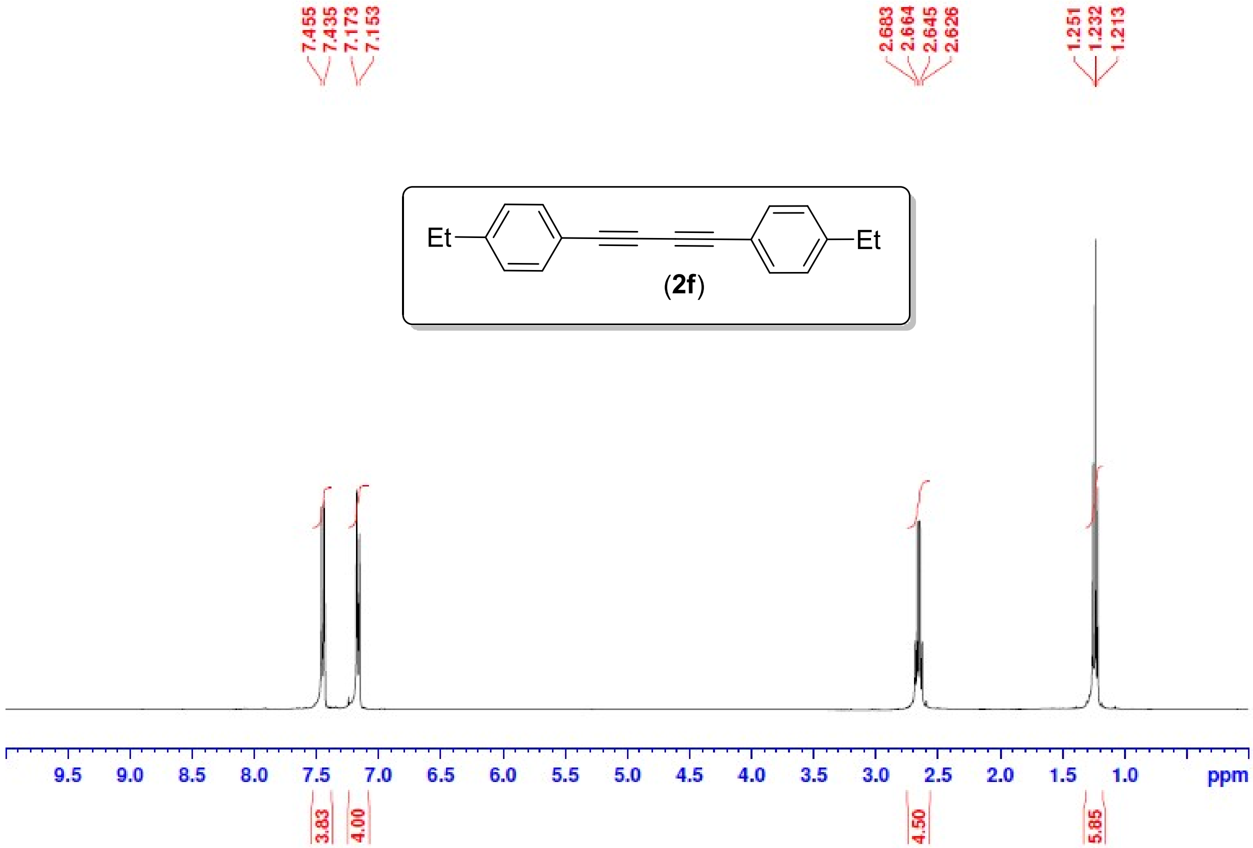

tBu
tBu

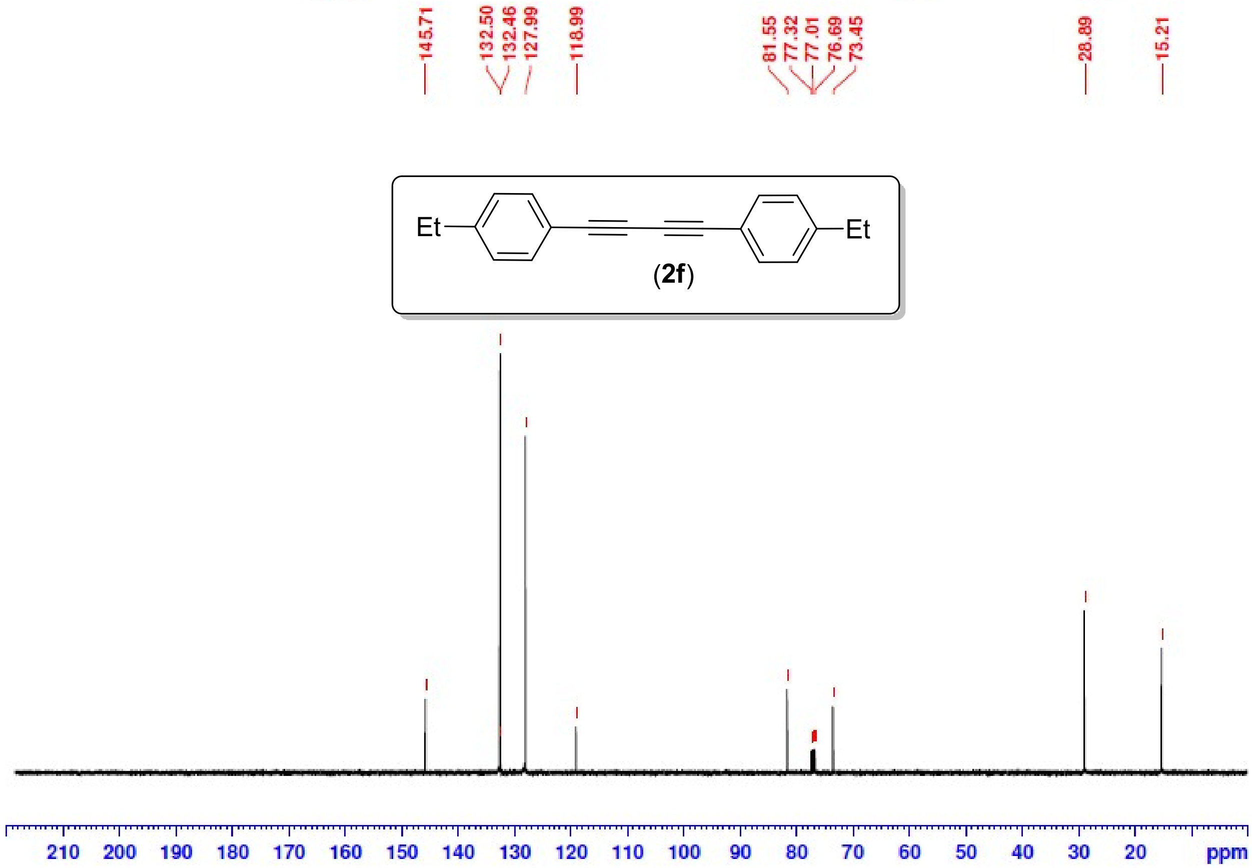
(**2d**)

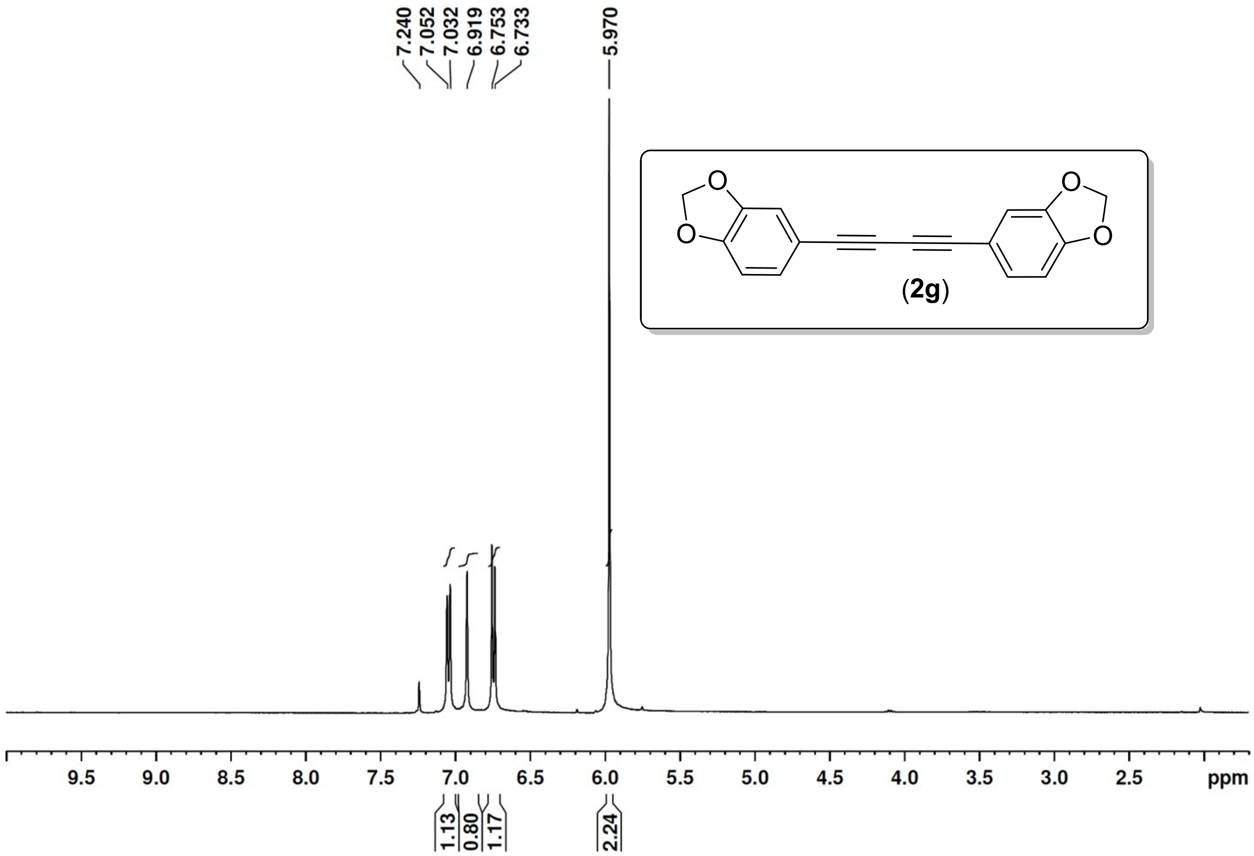


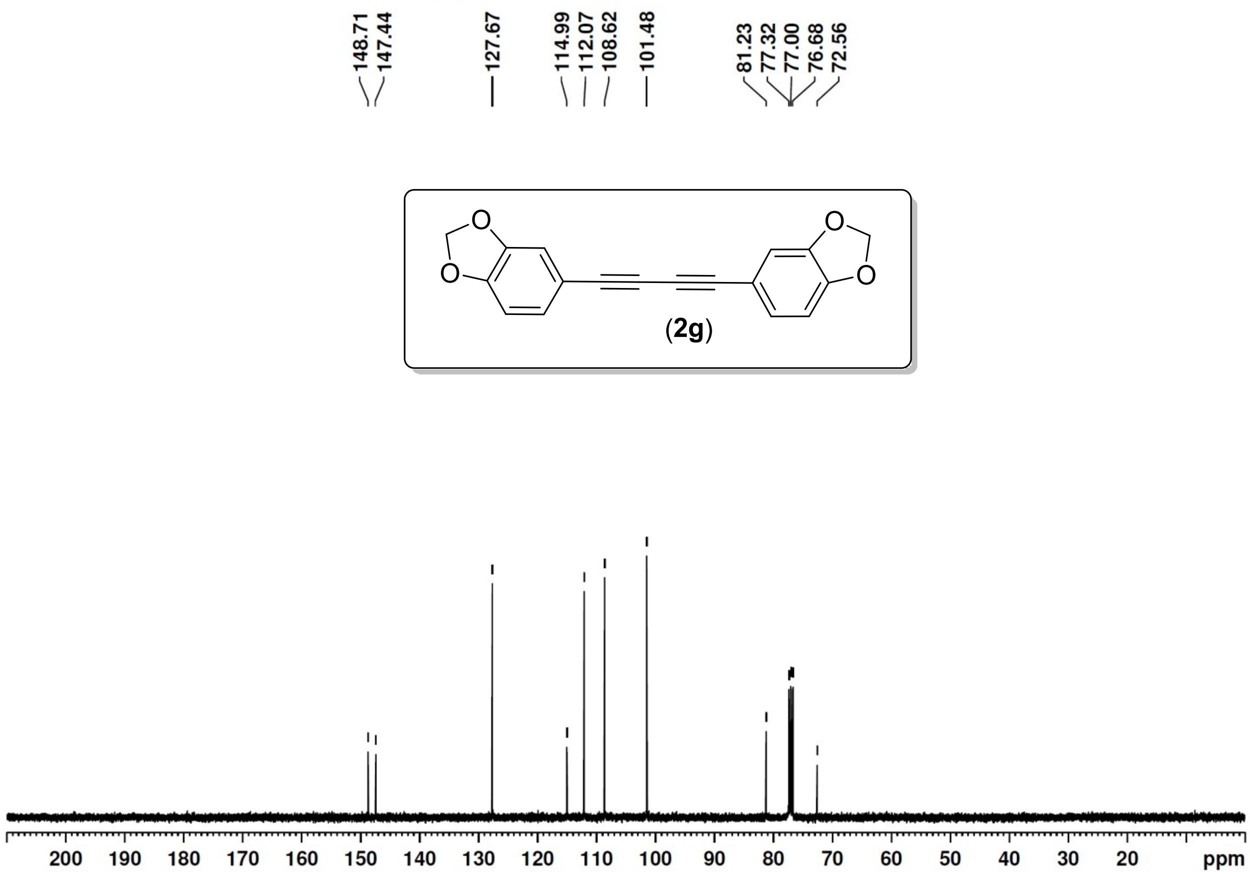

7.431
7.417
7.240
7.140
7.126
2.616
2.603
2.590
1.605
1.592
1.579
1.575
1.568
1.566
1.554
1.543
1.370
1.358
1.345
1.333
1.320
1.308
0.929
0.917
0.905
nBu
nBu
(2e)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.06
4.00
4.63
4.49
4.21
6.08

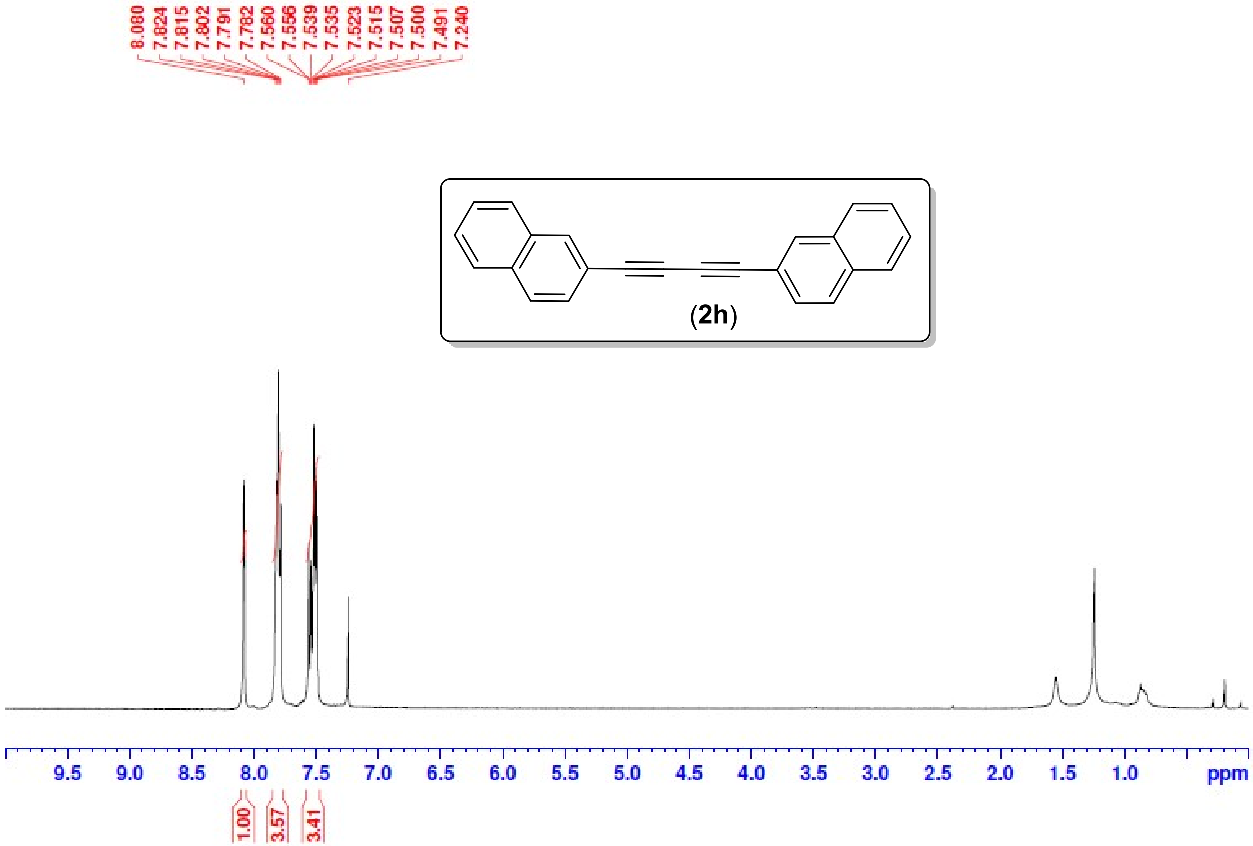

144.44
132.38
128.54
118.96
81.56
77.21
77.00
76.79
73.46
35.66
33.28
22.28
13.89
nBu
nBu
(2e)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

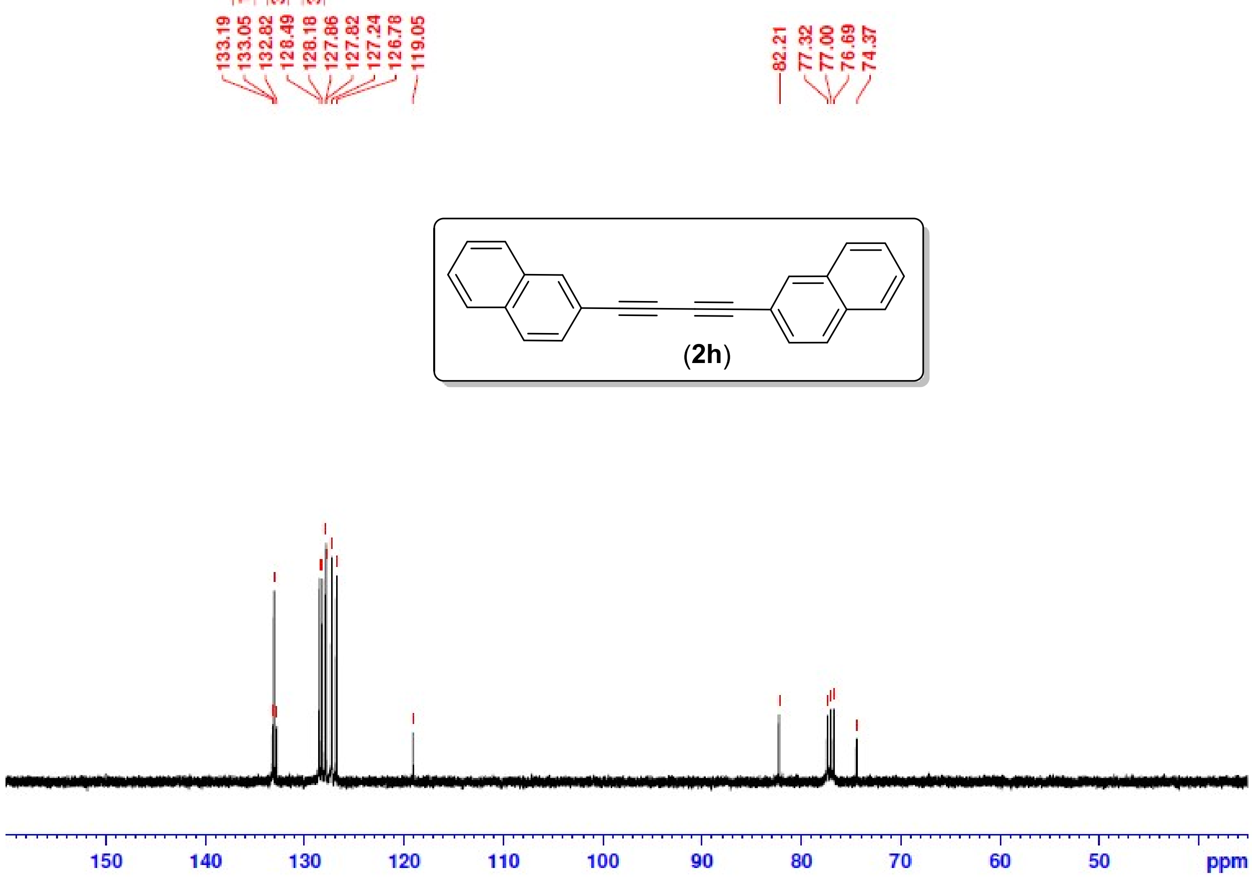

7.455
7.435
7.173
7.153
2.683
2.664
2.645
2.626
1.251
1.232
1.213
Et
Et
(2f)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.83
4.00
4.50
5.85

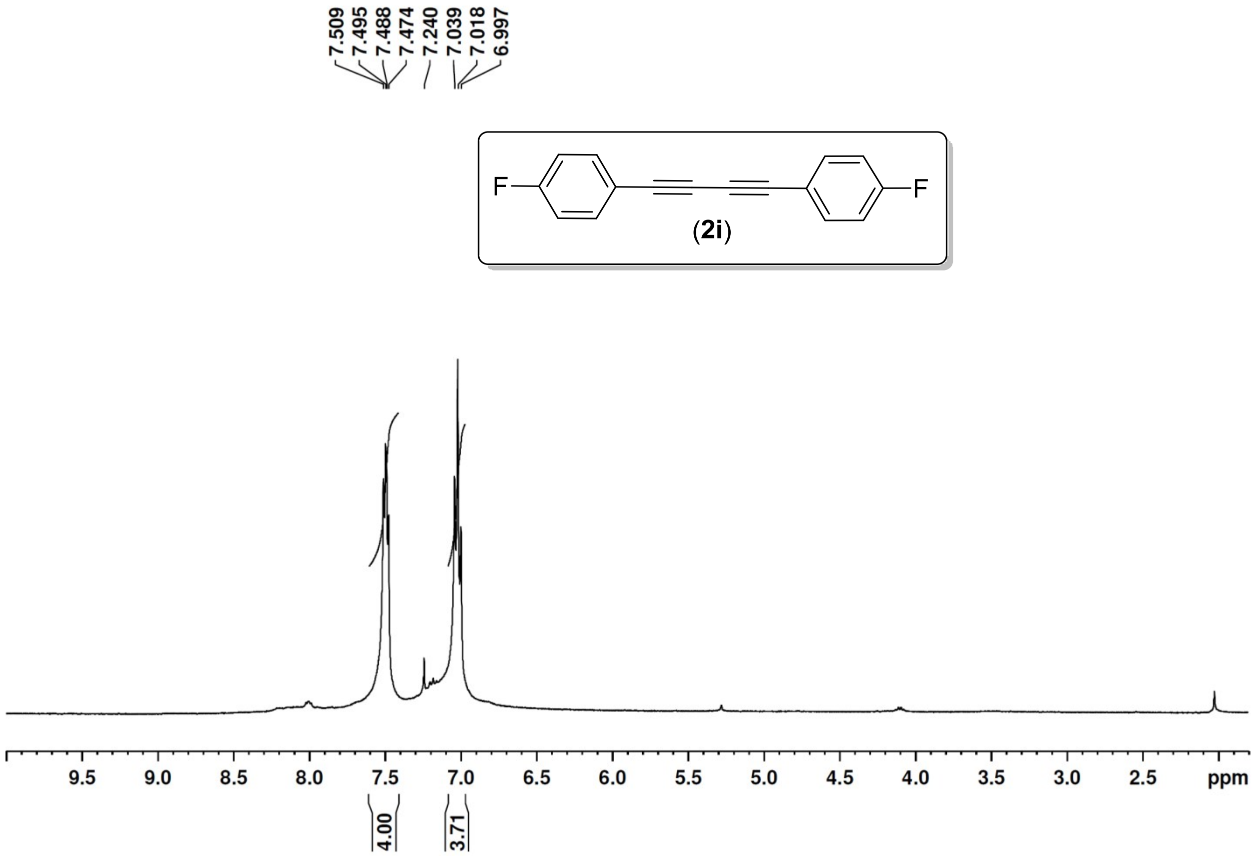

145.71
132.50
132.46
127.99
118.99
81.55
77.32
77.01
76.69
73.45
28.89
15.21
Et
Et
(2f)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

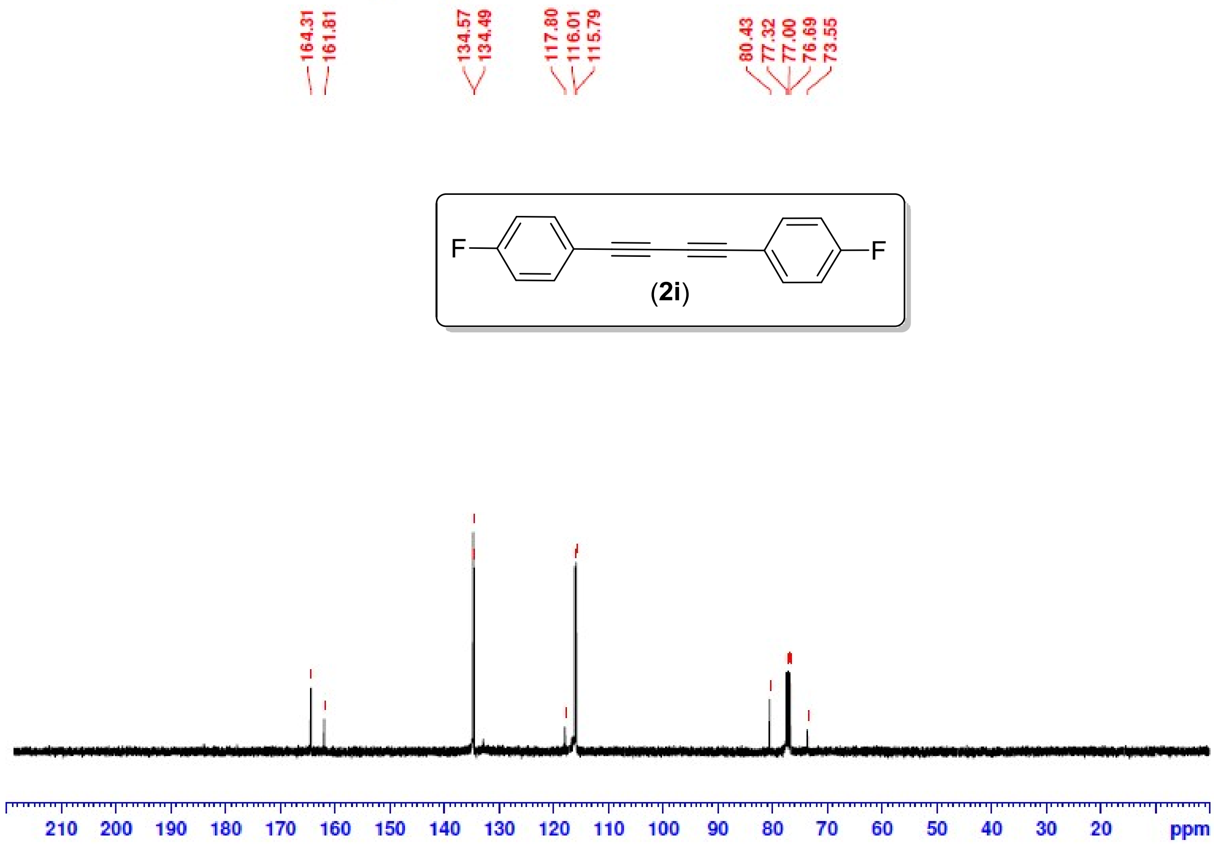

7.240
7.052
7.032
6.919
6.753
6.733
5.970
(2g)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.13
0.80
1.17
2.24

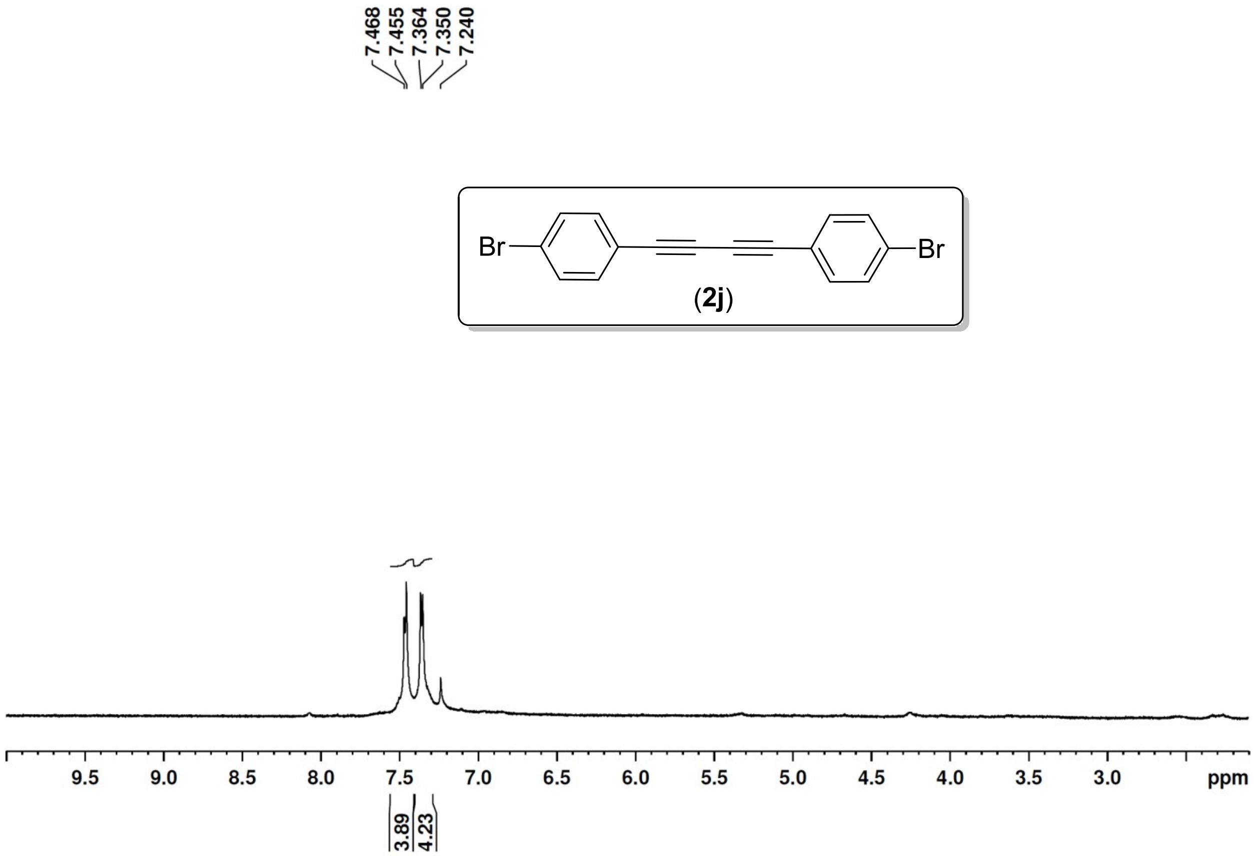

148.71
147.44
127.67
114.99
112.07
108.62
101.48
81.23
77.32
77.00
76.68
72.56
(2g)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

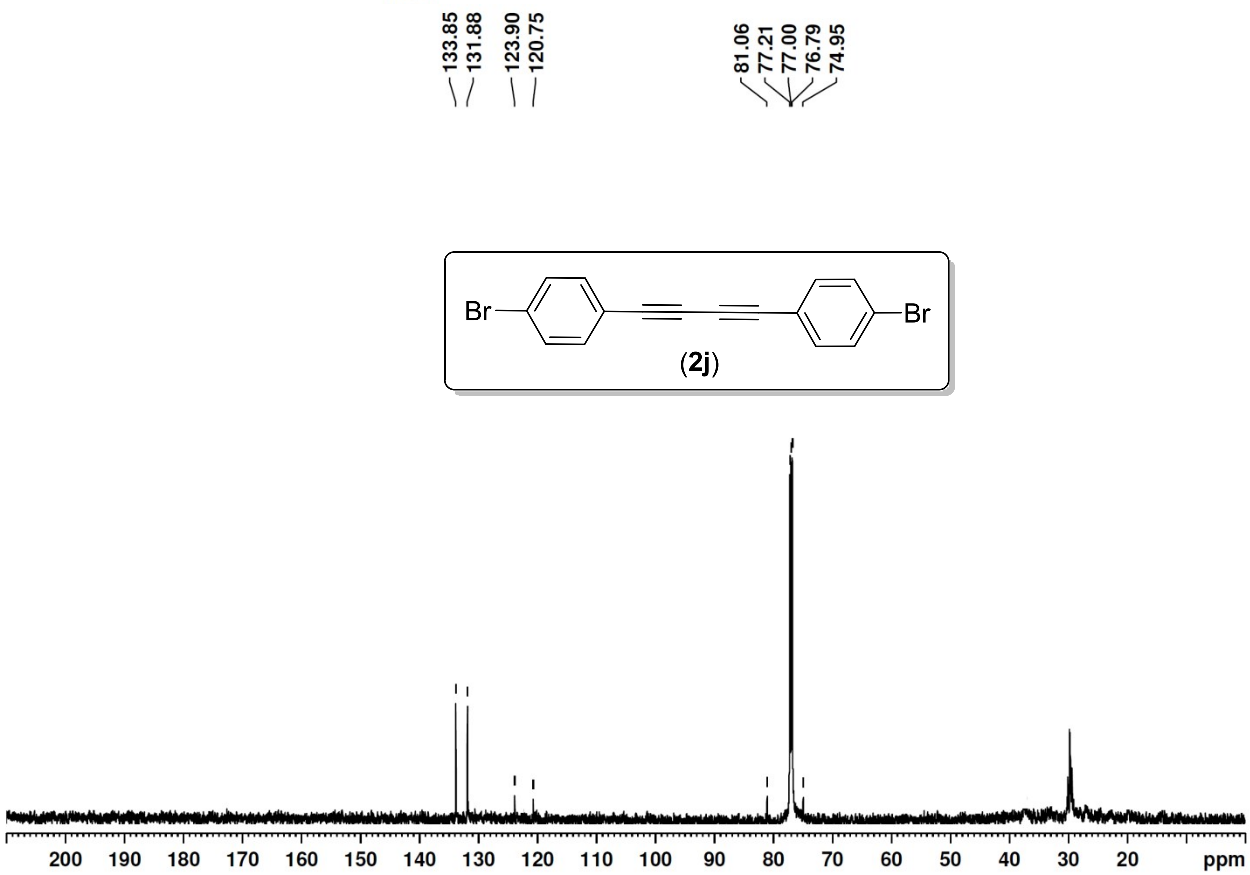

8.080
7.824
7.815
7.802
7.791
7.782
7.560
7.556
7.539
7.535
7.523
7.515
7.507
7.500
7.491
7.240
(2h)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
3.57
3.41

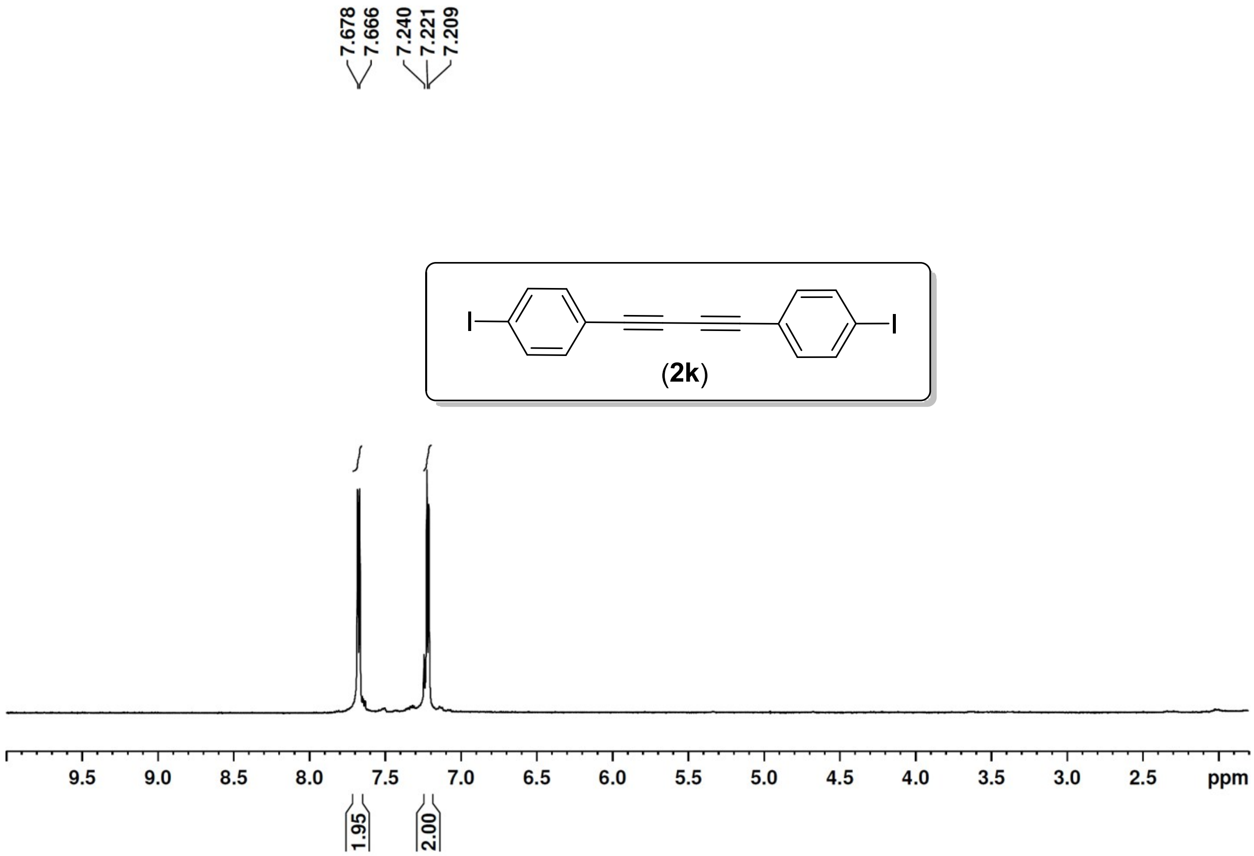

133.19
133.05
132.82
128.49
128.18
127.86
127.82
127.24
126.78
119.05
82.21
77.32
77.00
76.69
74.37
(2h)
150 140 130 120 110 100 90 80 70 60 50 ppm

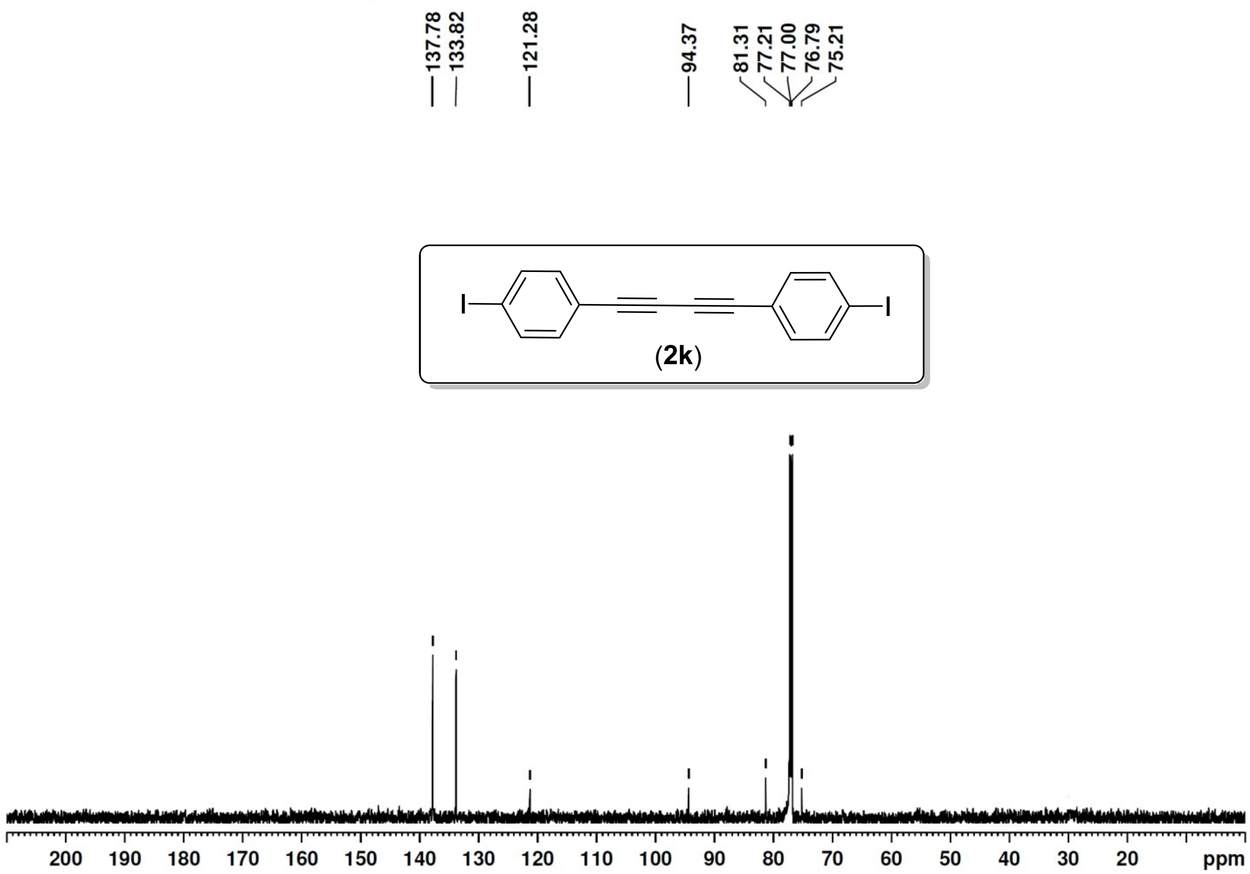

7.509
7.495
7.488
7.474
7.240
7.039
7.018
6.997
F
F
(2i)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
4.00
3.71

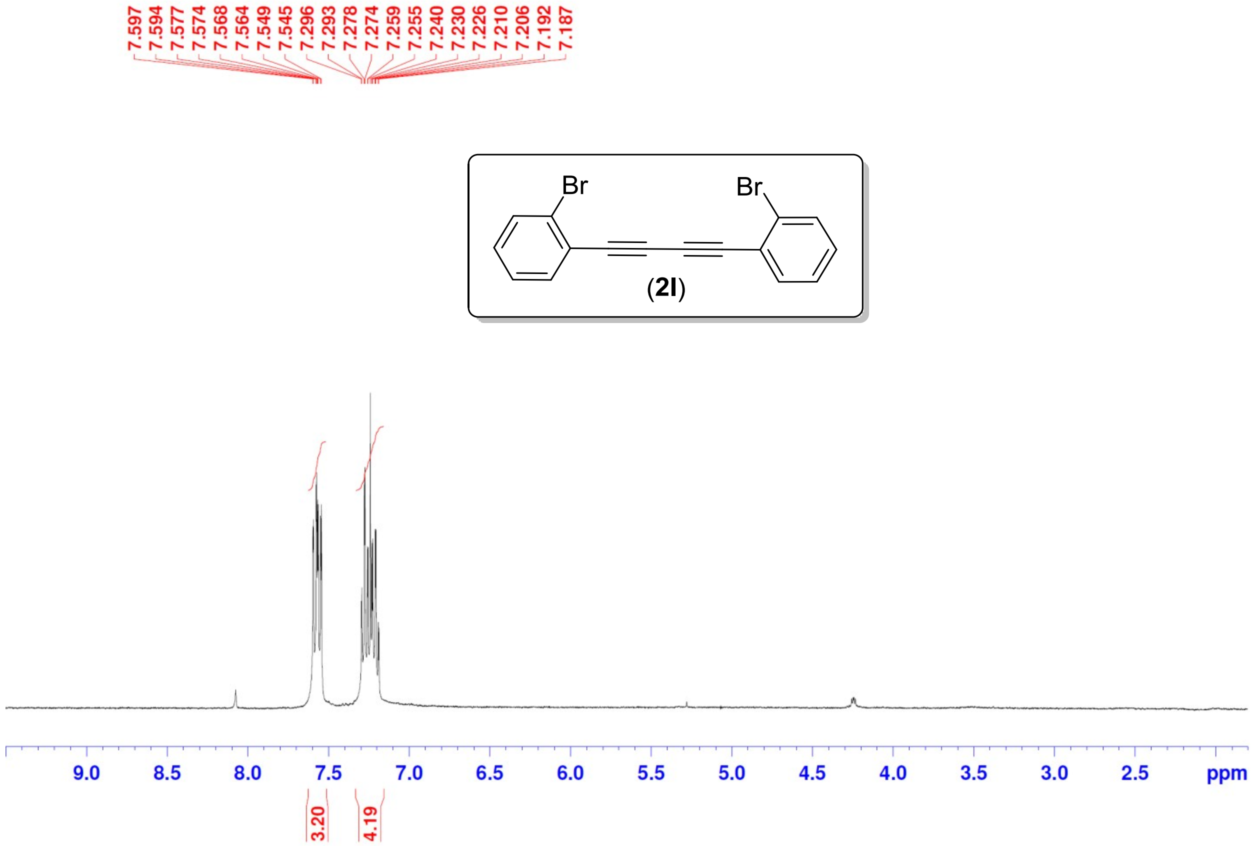

164.31
161.81
134.57
134.49
117.80
116.01
115.79
80.43
77.32
77.00
76.69
73.55
F
F
(2i)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

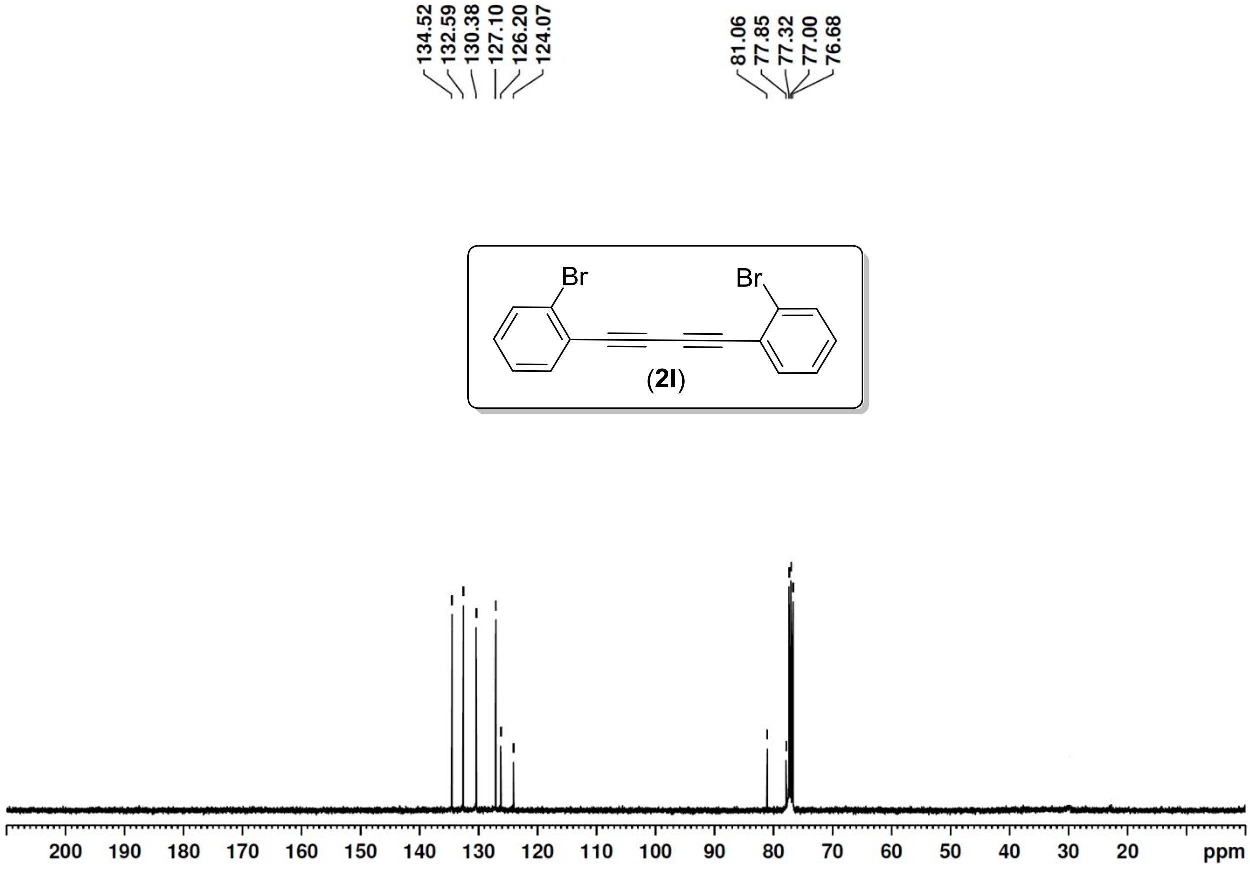

7.468
7.455
7.364
7.350
7.240
Br
Br
(2j)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
3.89
4.23

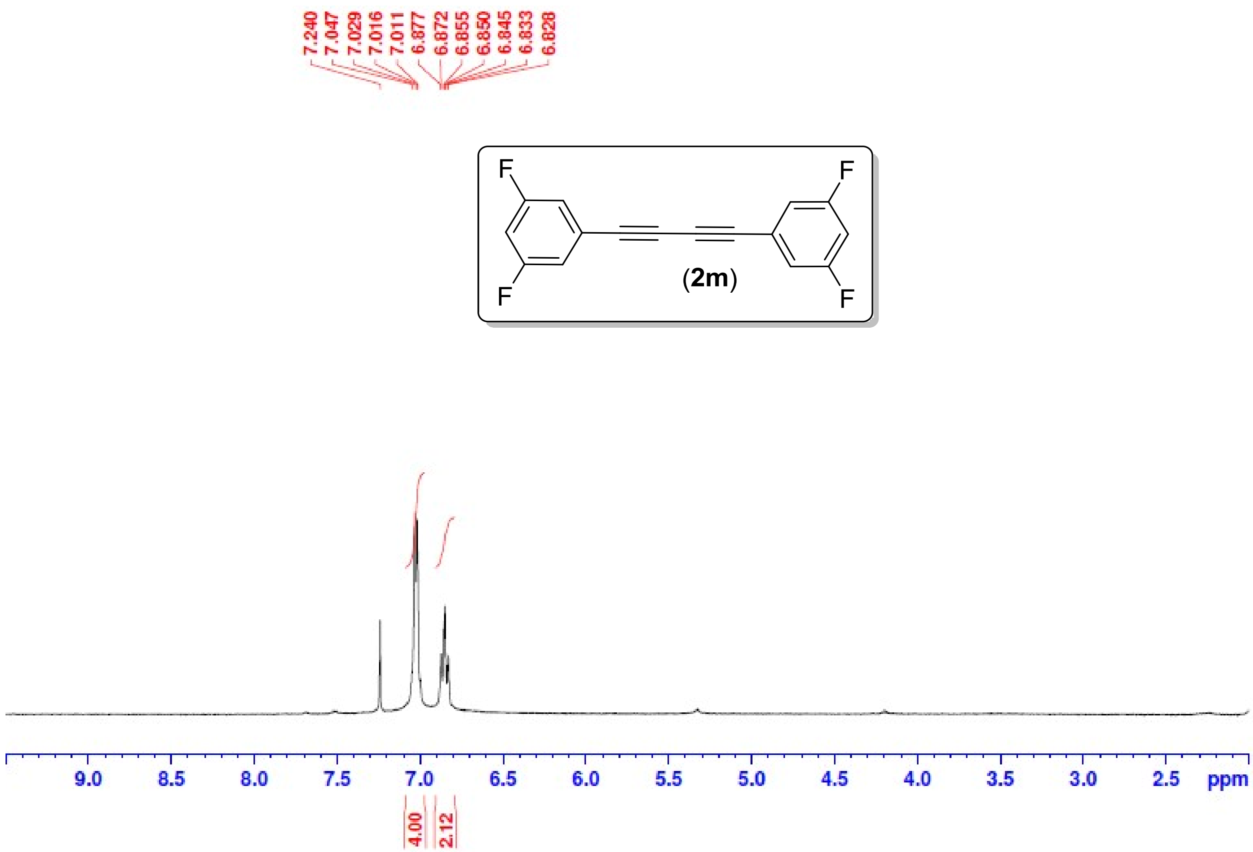

133.85
131.88
123.90
120.75
81.06
77.21
77.00
76.79
74.95
Br
Br
(2j)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

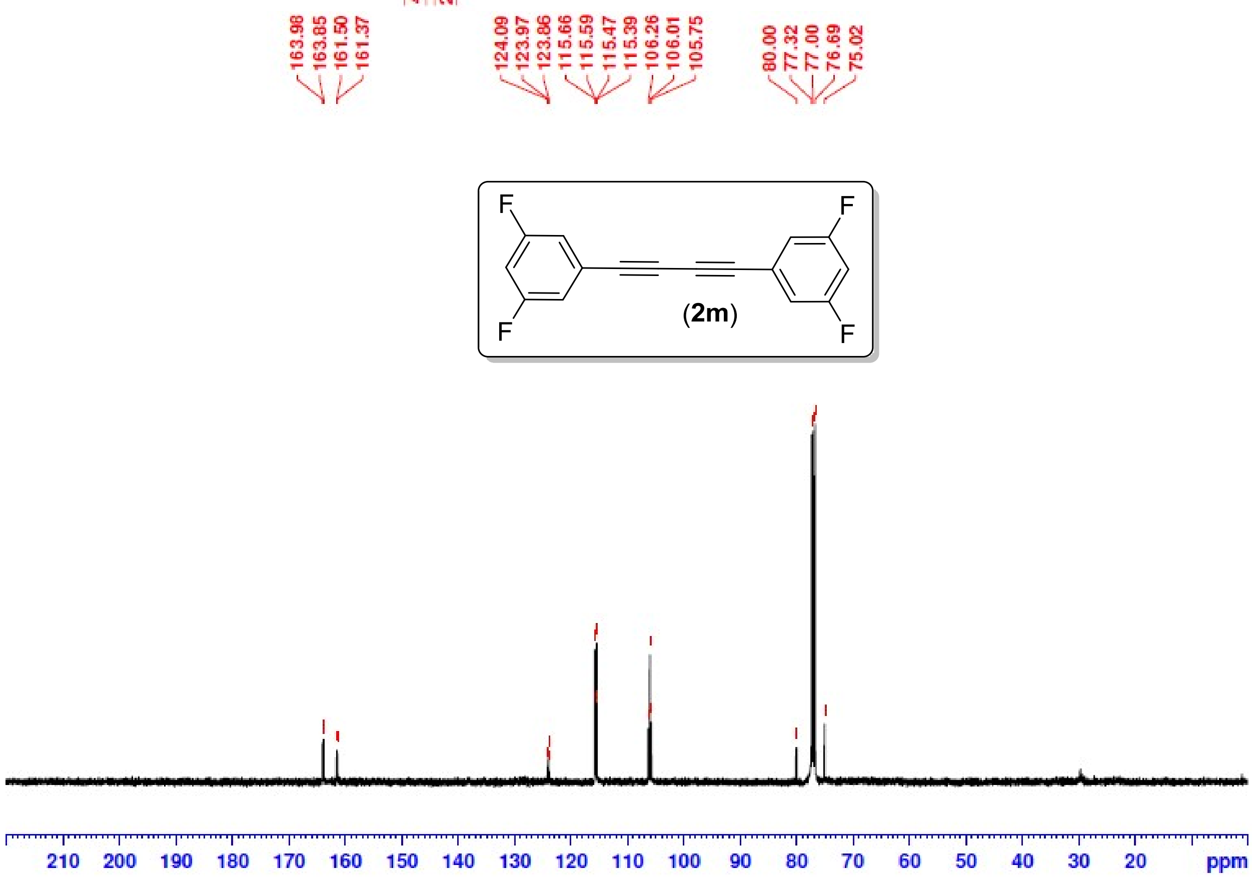

7.678
7.666
7.240
7.221
7.209
(2k)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.95
2.00

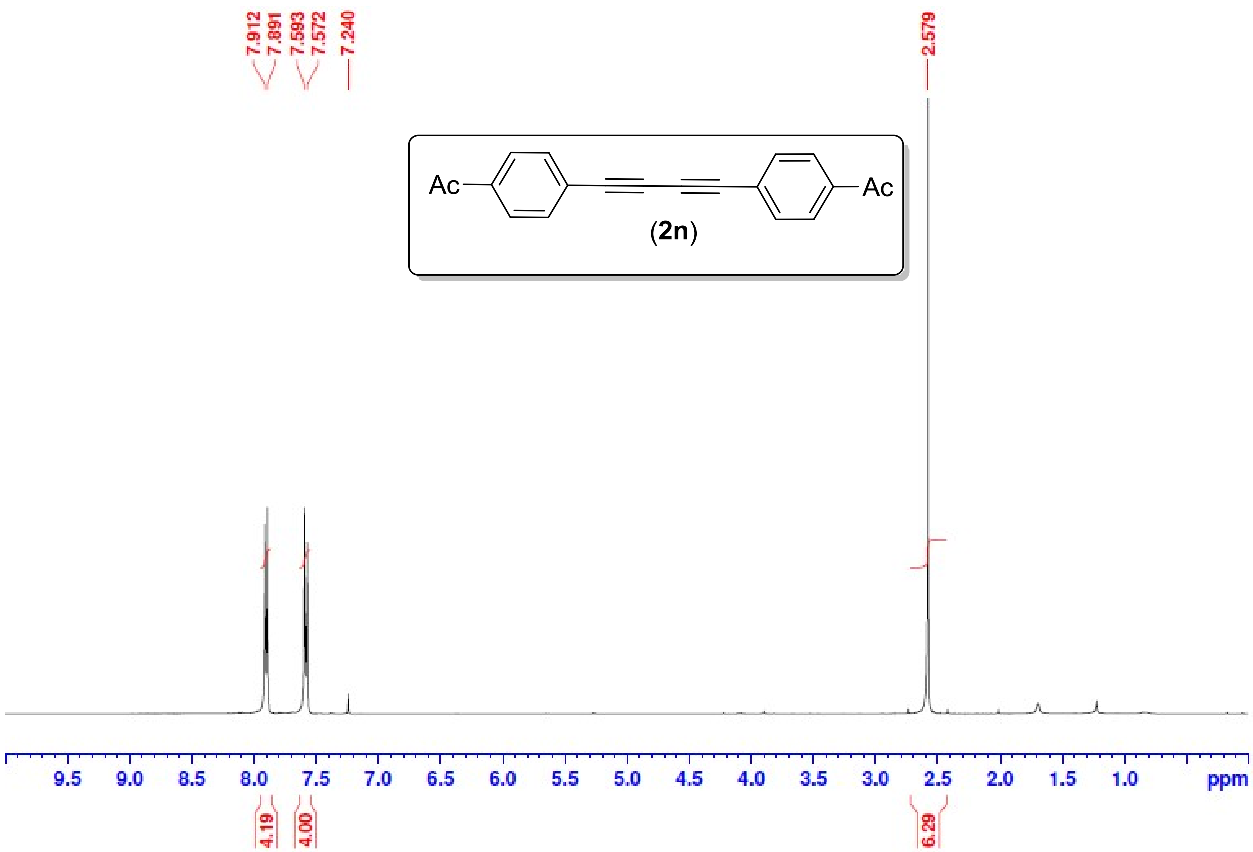

137.78
133.82
121.28
94.37
81.31
77.21
77.00
76.79
75.21
(2k)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

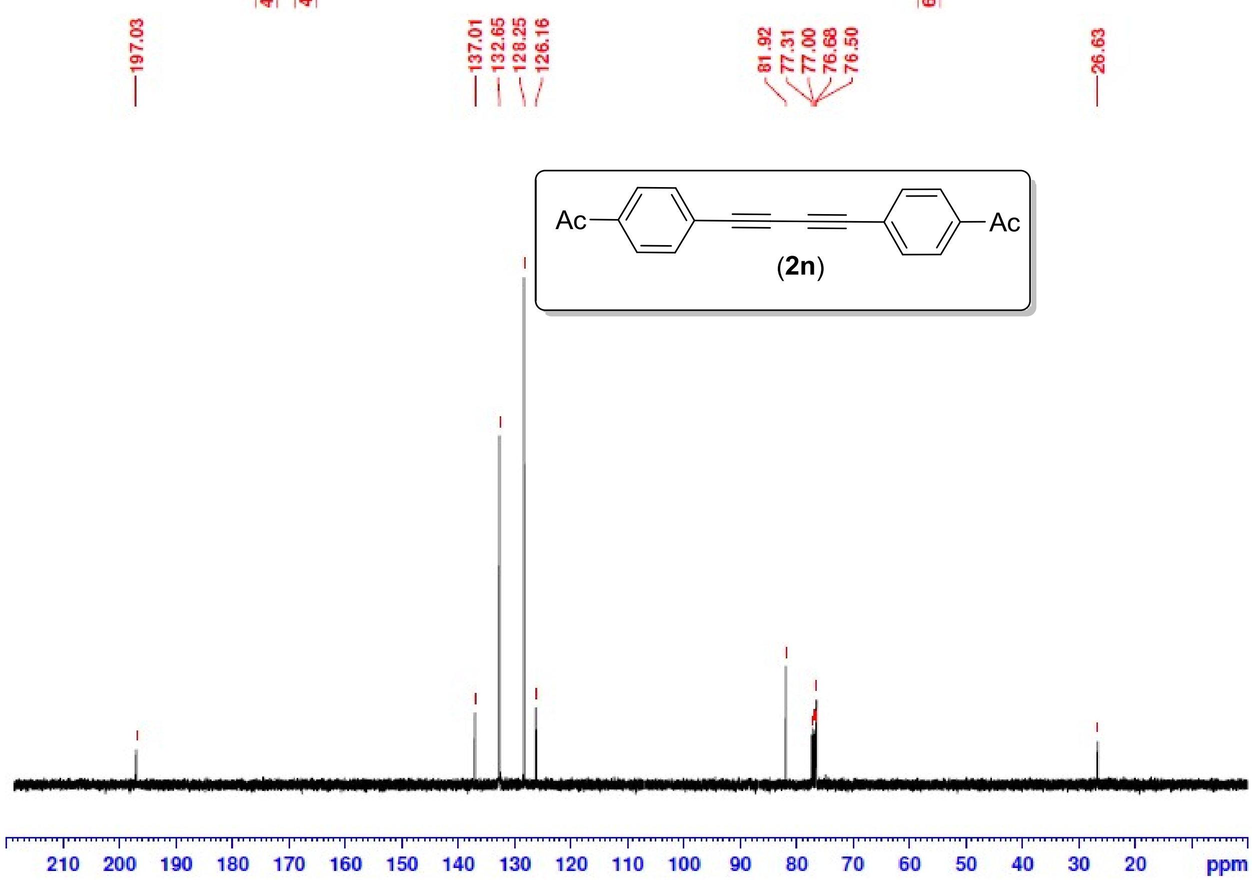

7.597
7.594
7.577
7.574
7.568
7.564
7.549
7.545
7.296
7.293
7.278
7.274
7.259
7.255
7.240
7.230
7.226
7.210
7.206
7.192
7.187
Br
Br
(2l)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
3.20
4.19

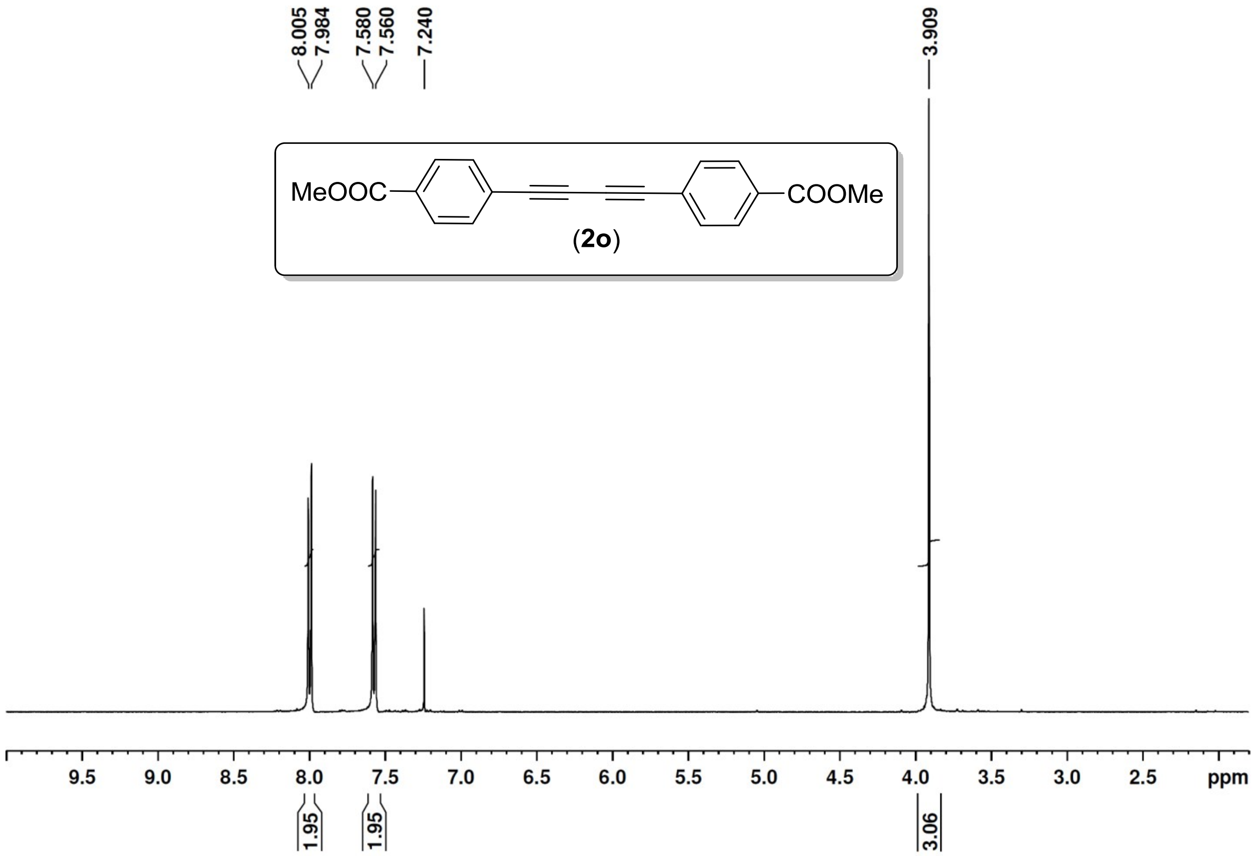

134.52
132.59
130.38
127.10
126.20
124.07
81.06
77.85
77.32
77.00
76.68
Br
Br
(2l)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

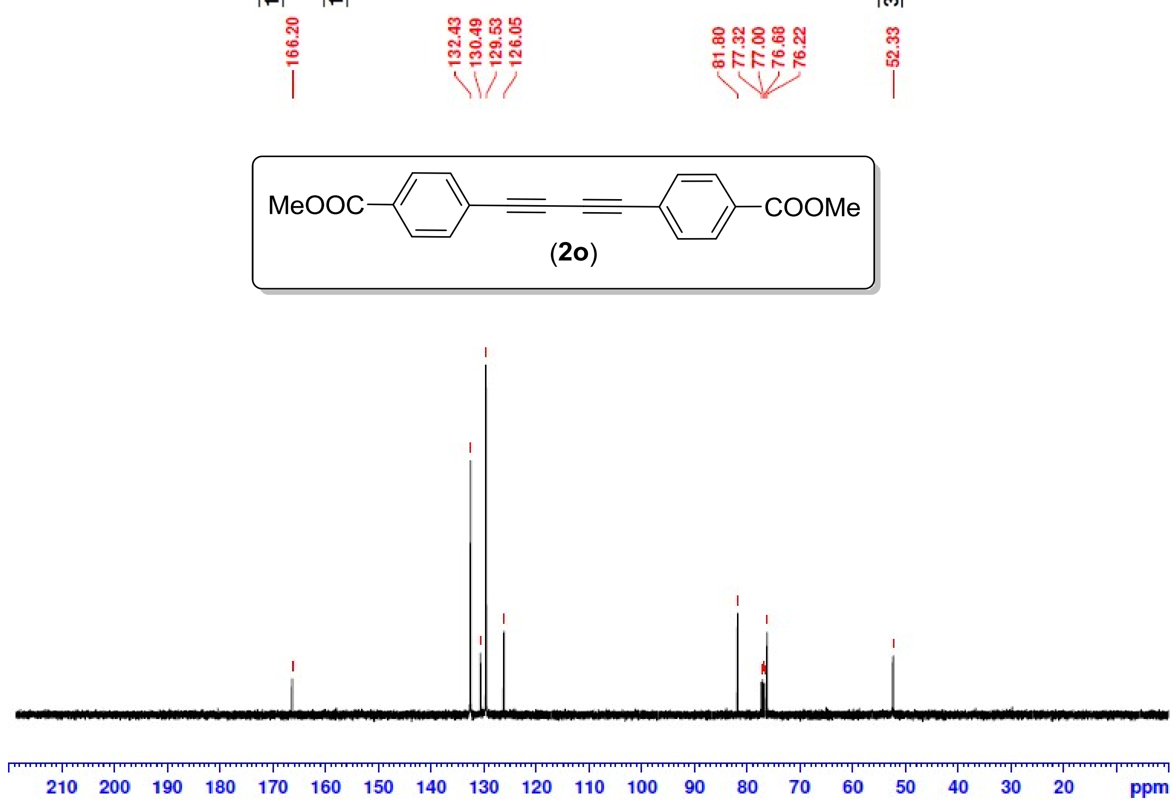

7.240
7.047
7.029
7.016
7.011
6.877
6.872
6.855
6.850
6.845
6.833
6.828
F
F
F
F
(2m)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
4.00
2.12

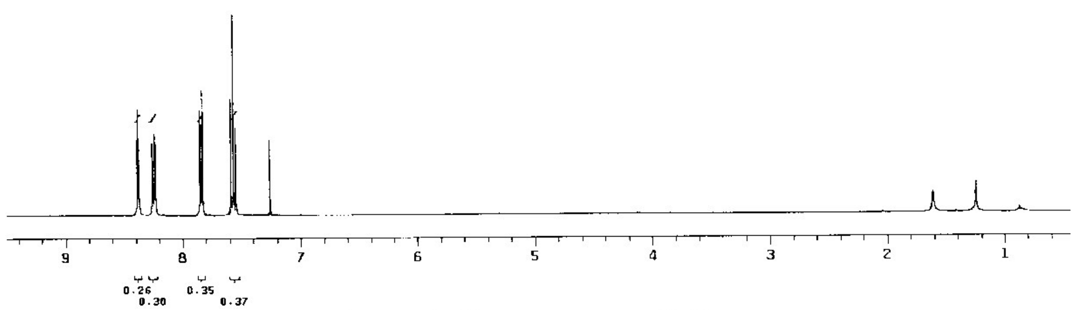

163.98
163.85
161.50
161.37
124.09
123.97
123.86
115.66
115.59
115.47
115.39
106.26
106.01
105.75
80.00
77.32
77.00
76.69
75.02
F
F
F
F
(2m)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.912
7.891
7.593
7.572
7.240
2.579
Ac
Ac
(2n)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.19
4.00
6.29


197.03
137.01
132.65
128.25
126.16
81.92
77.31
77.00
76.68
76.50
26.63
Ac
Ac
(2n)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

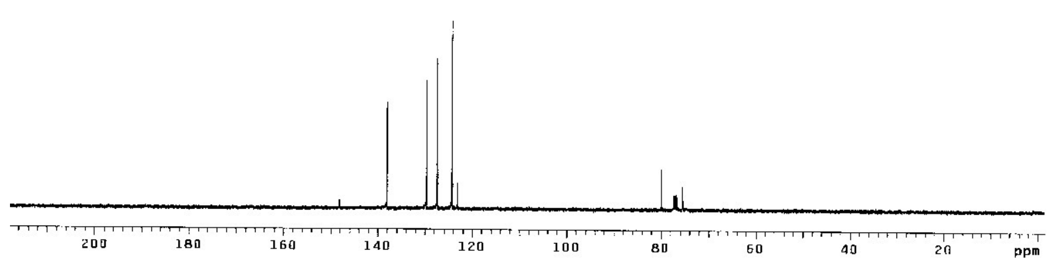

8.005
7.984
7.580
7.560
7.240
3.909
MeOOC
COOMe
(2o)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.95
1.95
3.06

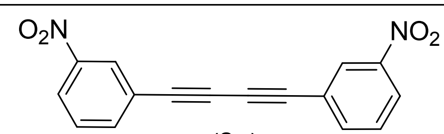

166.20
132.43
130.49
129.53
126.05
81.80
77.32
77.00
76.68
76.22
52.33
MeOOC
COOMe
(2o)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.387 8.382 8.379 8.262 8.260 8.256 8.253 8.241 8.239 8.236 8.233 7.854 7.851 7.848 7.835 7.831 7.829 7.587 7.568 7.548 7.547 7.259
1340-1homo
exp1 std1h
SAMPLE
date Jan 20 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.444
tn H1
at 1.995
np 23964
sw 6006.0
fb 3400
bs 4
tpwr 57
pw 7.0
d1 1.000
tof 0
nt 1000
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -200.2
wp 4004.1
vs 200
sc 0
wc 250
hzmm 16.02
is 52.35
rfl 1030.2
rfp 0
th 7
ins 2.000
nm cdc ph
DEC. & VT
dfrq 400.444
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
9 8 7 6 5 4 3 2 1
0.26 0.30 0.35 0.37

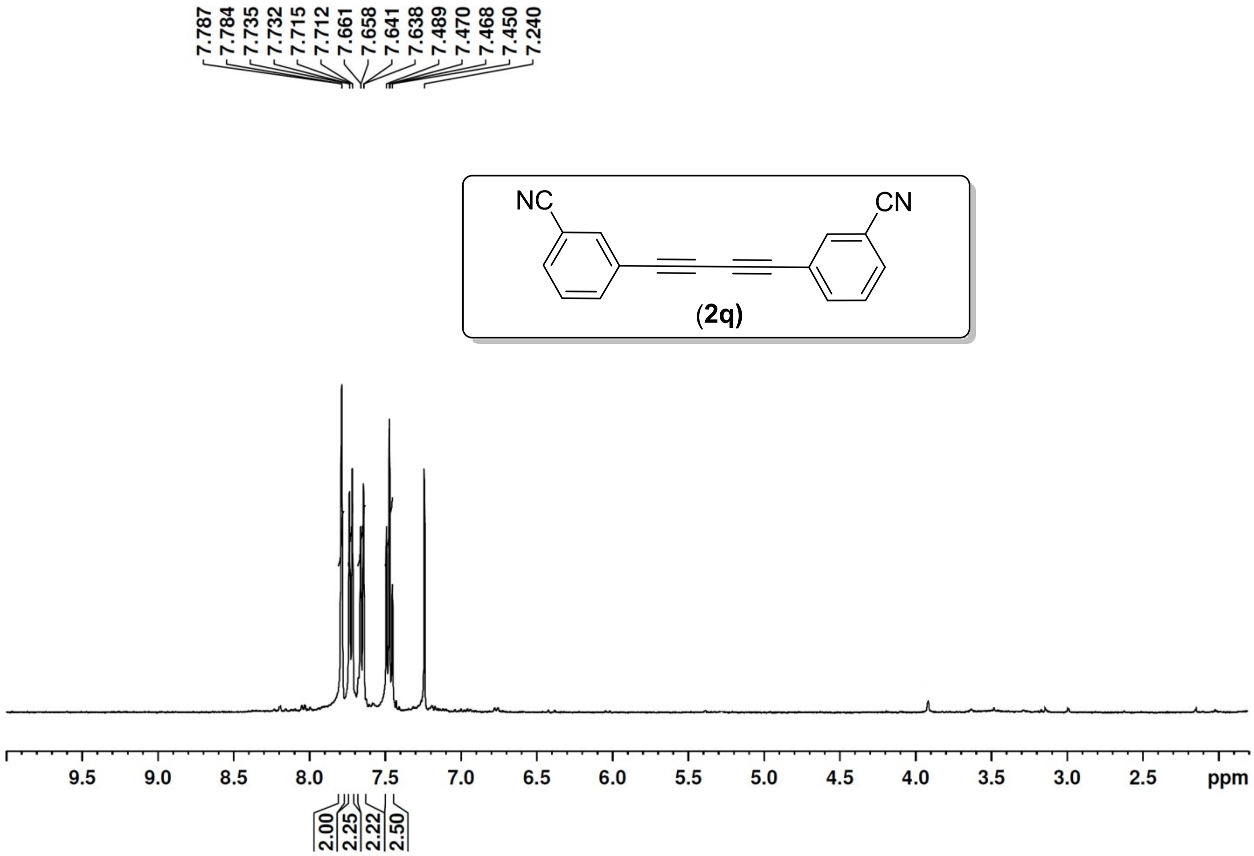

O2N
NO2

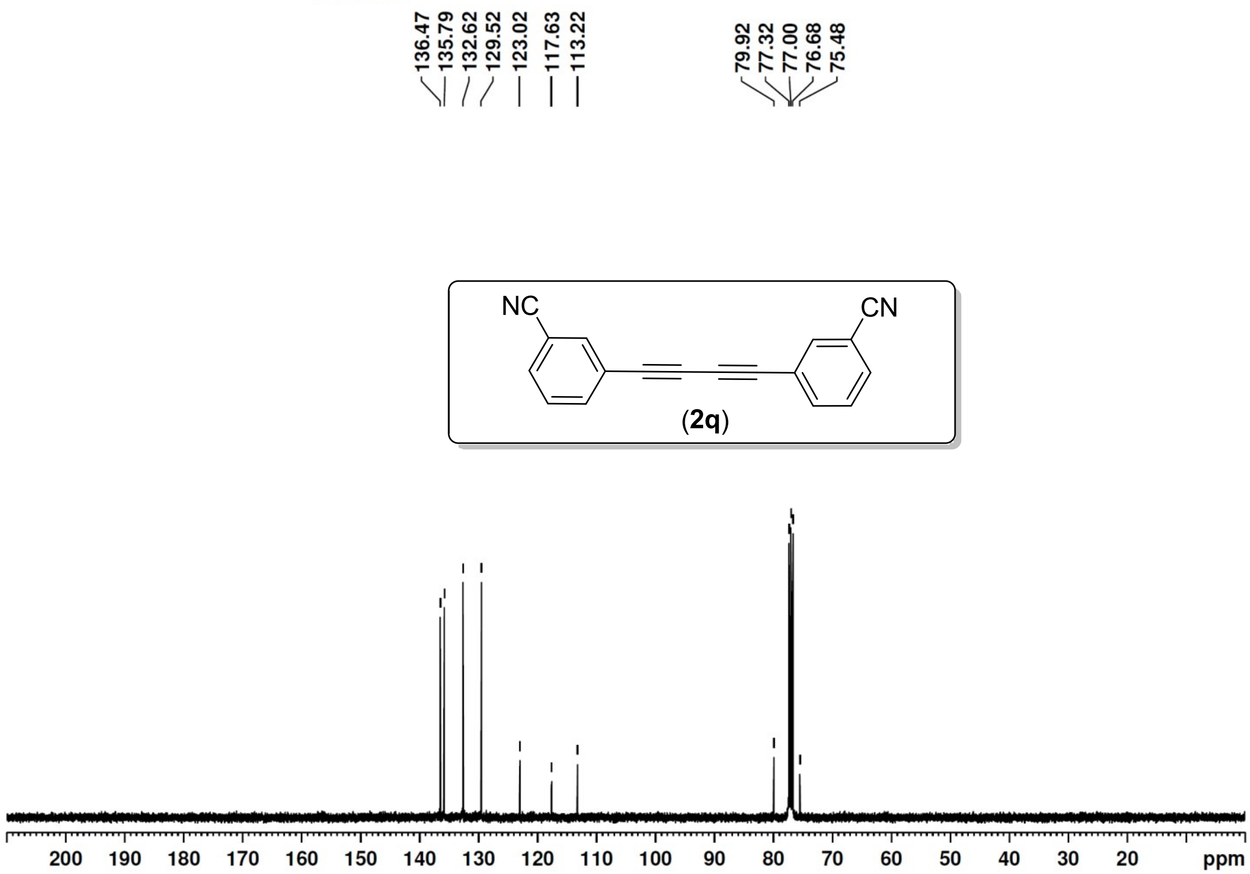
(**2p**)

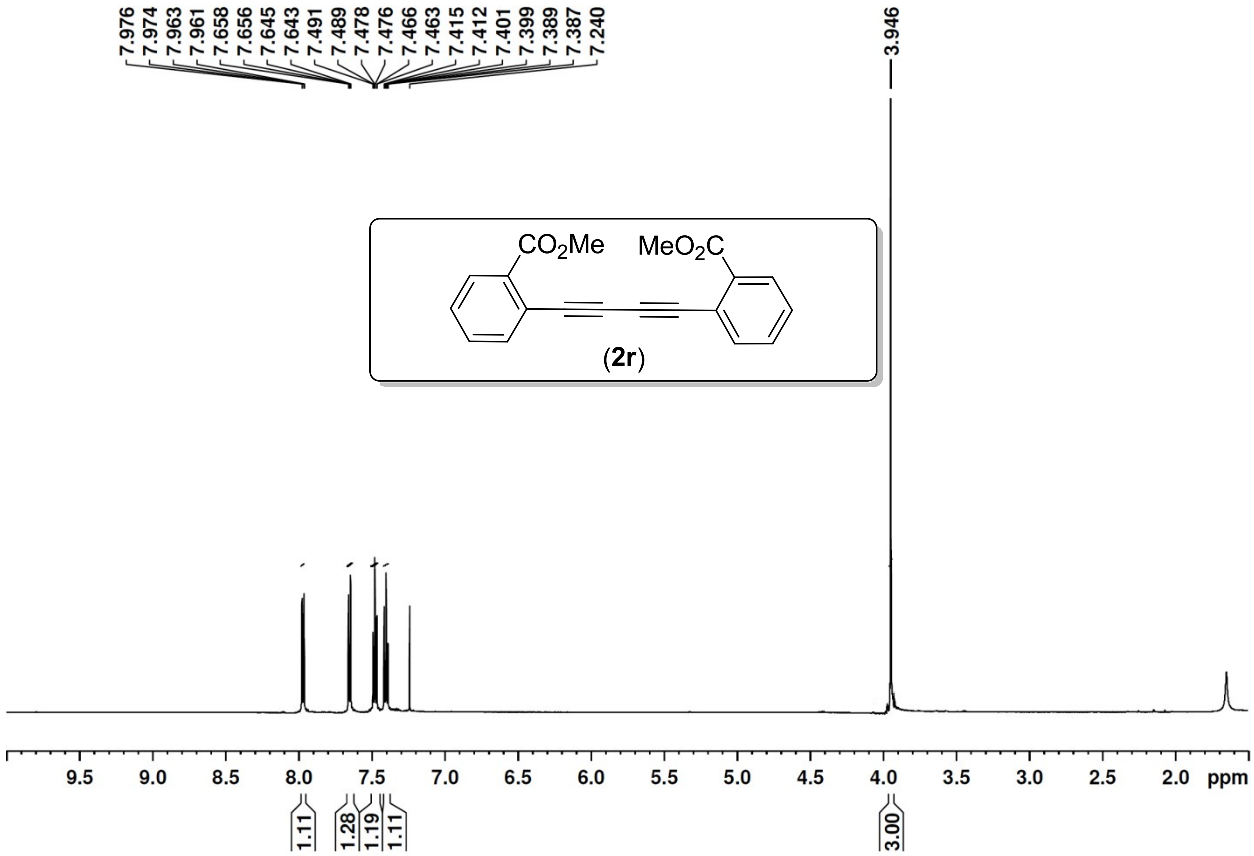

148.065
138.048
129.653
127.311
124.182
123.076
79.917
77.311
76.992
76.674
75.485
0.965
1340-12hom
exp6 std13c
SAMPLE
date Jan 21 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 100.701
tn C13
at 1.199
np 59968
sw 25000.0
fb 13800
bs 4
tpwr 58
pw 8.7
d1 0
tof 0
nt 100000
ct 332
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -160.0
wp 22151.9
vs 45
sc 0
wc 250
hzmm 88.61
is 500.00
rfl 10761.3
rfp 7753.2
th 2
ins 100.000
nm no ph
DEC. & VT
dfrq 400.444
dn H1
dpwr 39
dof 0
dm yyy
dmm w
dmf 9000
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
200 180 160 140 120 100 80 60 40 20 ppm

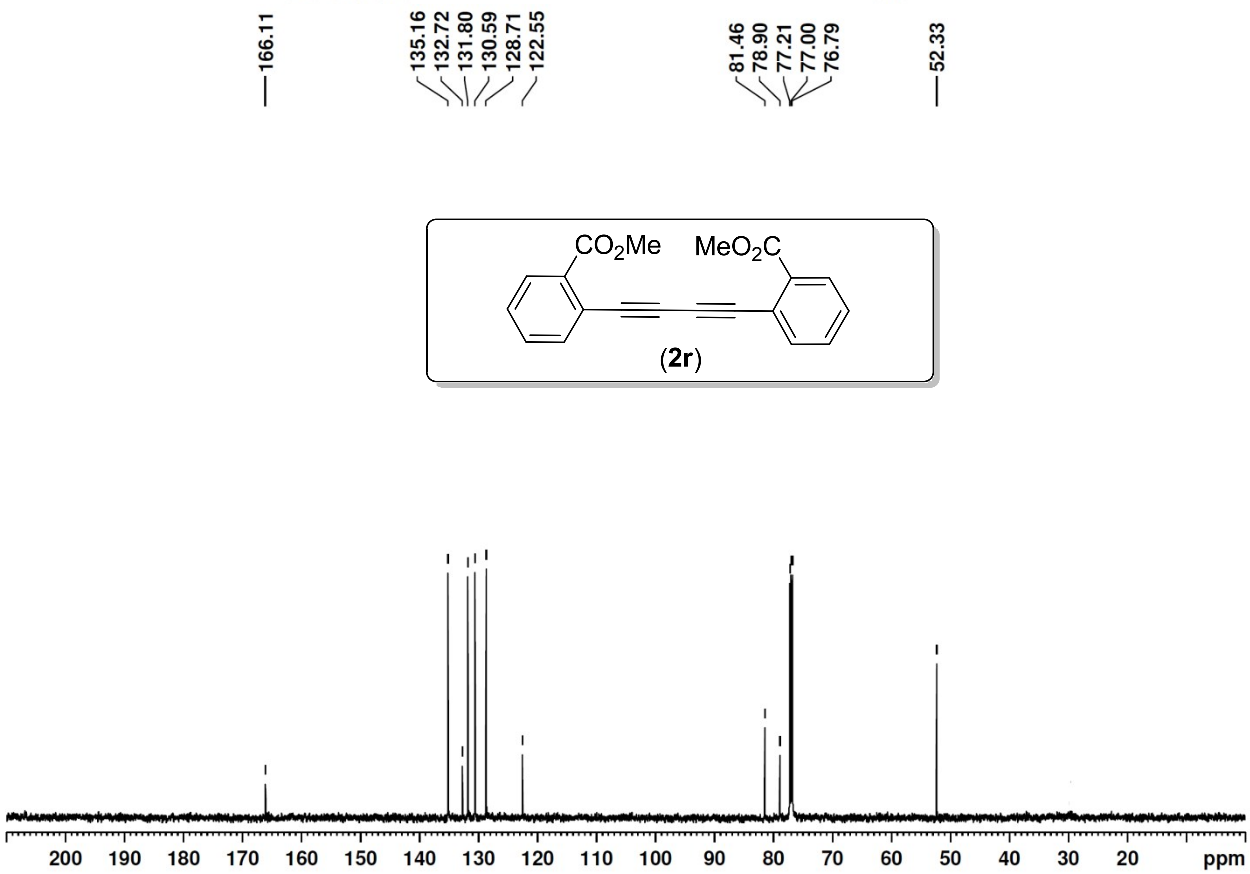

O2N
NO2

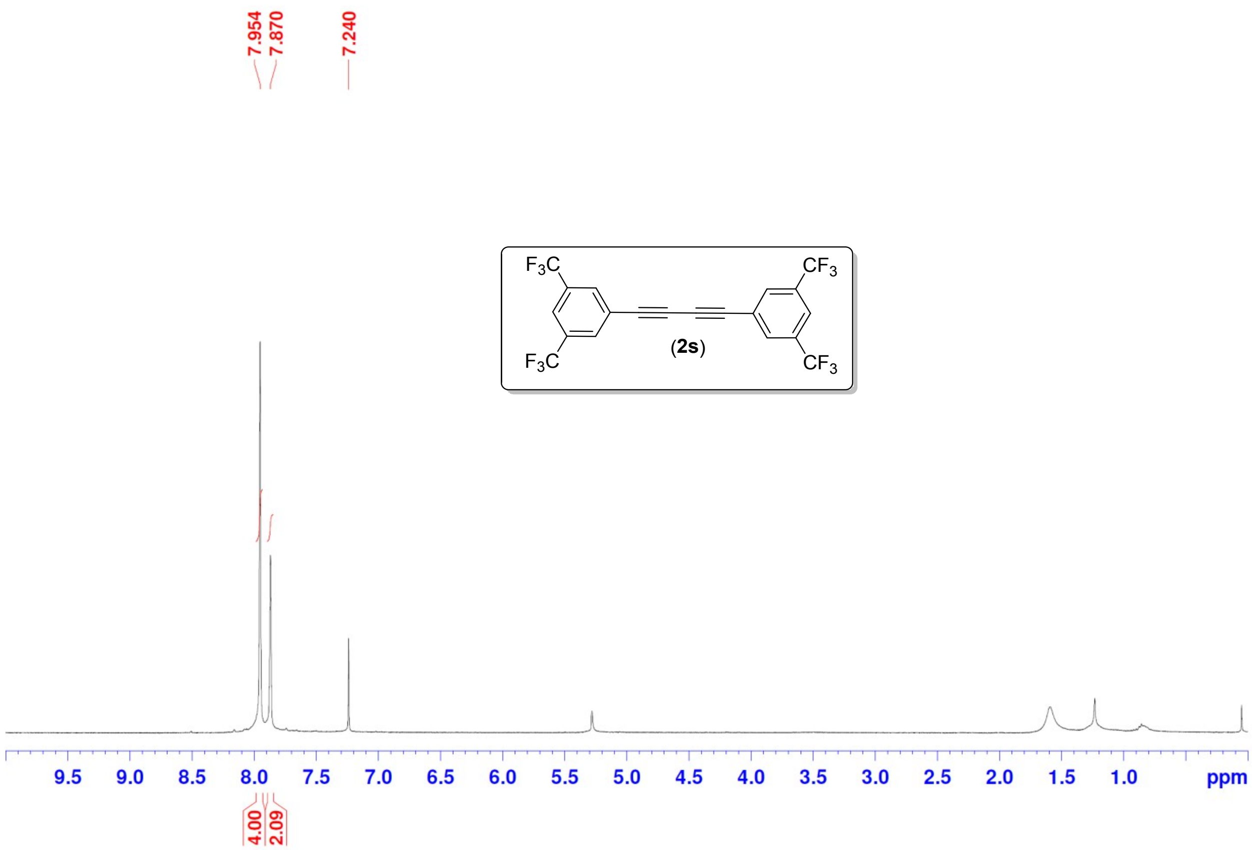
(**2p**)

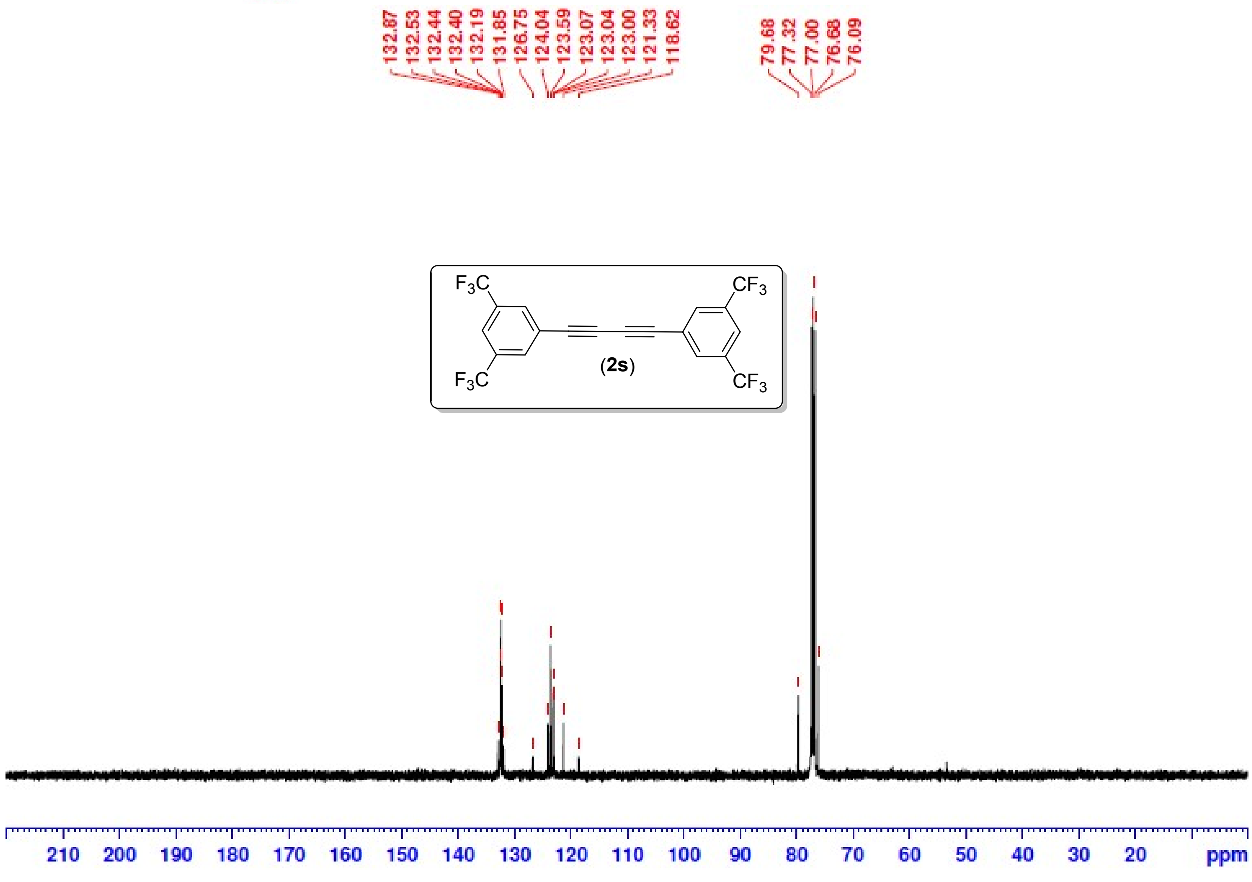

7.787
7.784
7.735
7.732
7.715
7.712
7.661
7.658
7.641
7.638
7.489
7.470
7.468
7.450
7.240
NC
CN
(2q)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
2.00
2.25
2.22
2.50

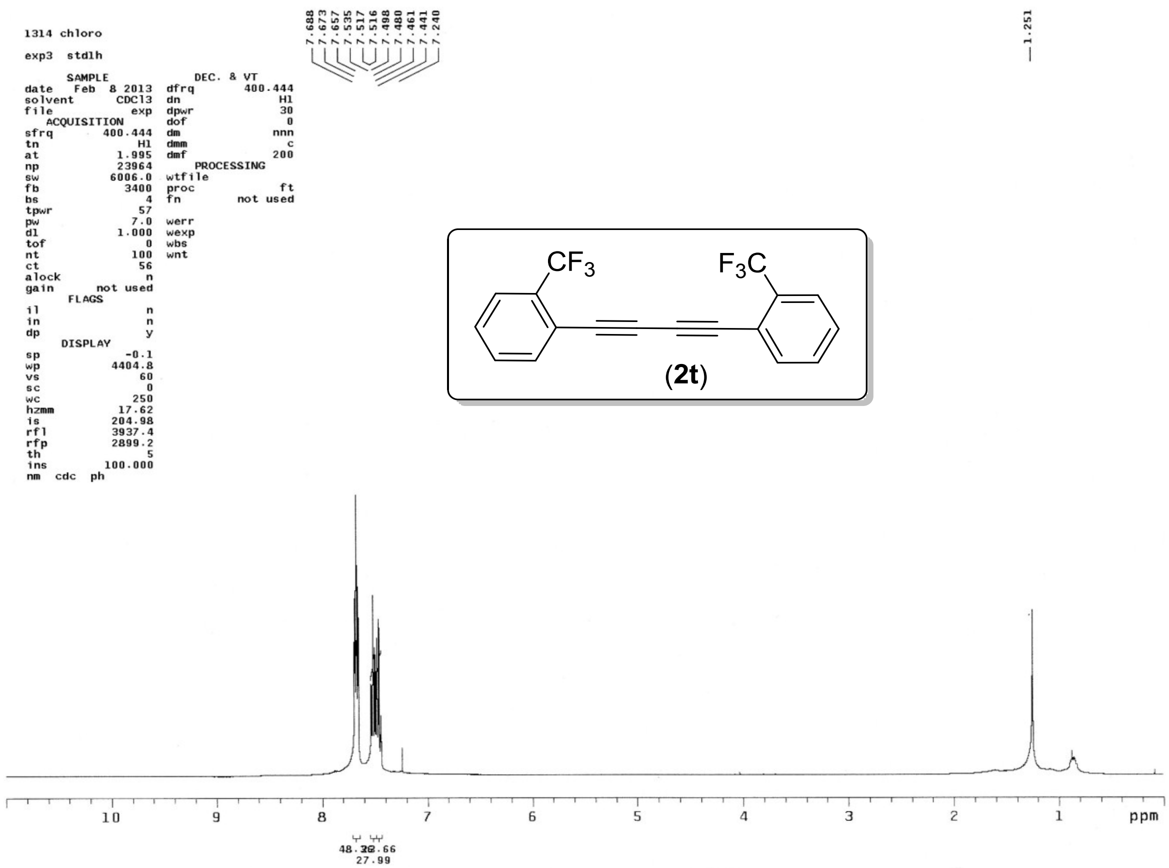
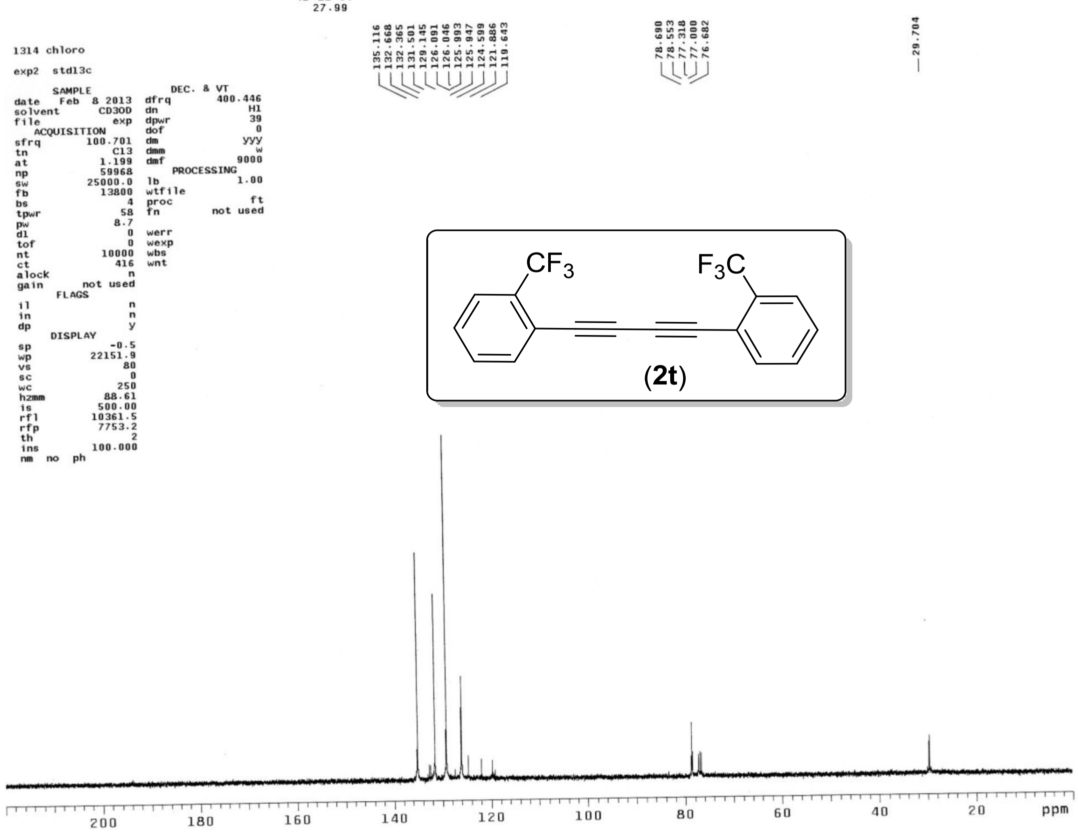

136.47
135.79
132.62
129.52
123.02
117.63
113.22
79.92
77.32
77.00
76.68
75.48
NC
CN
(2q)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

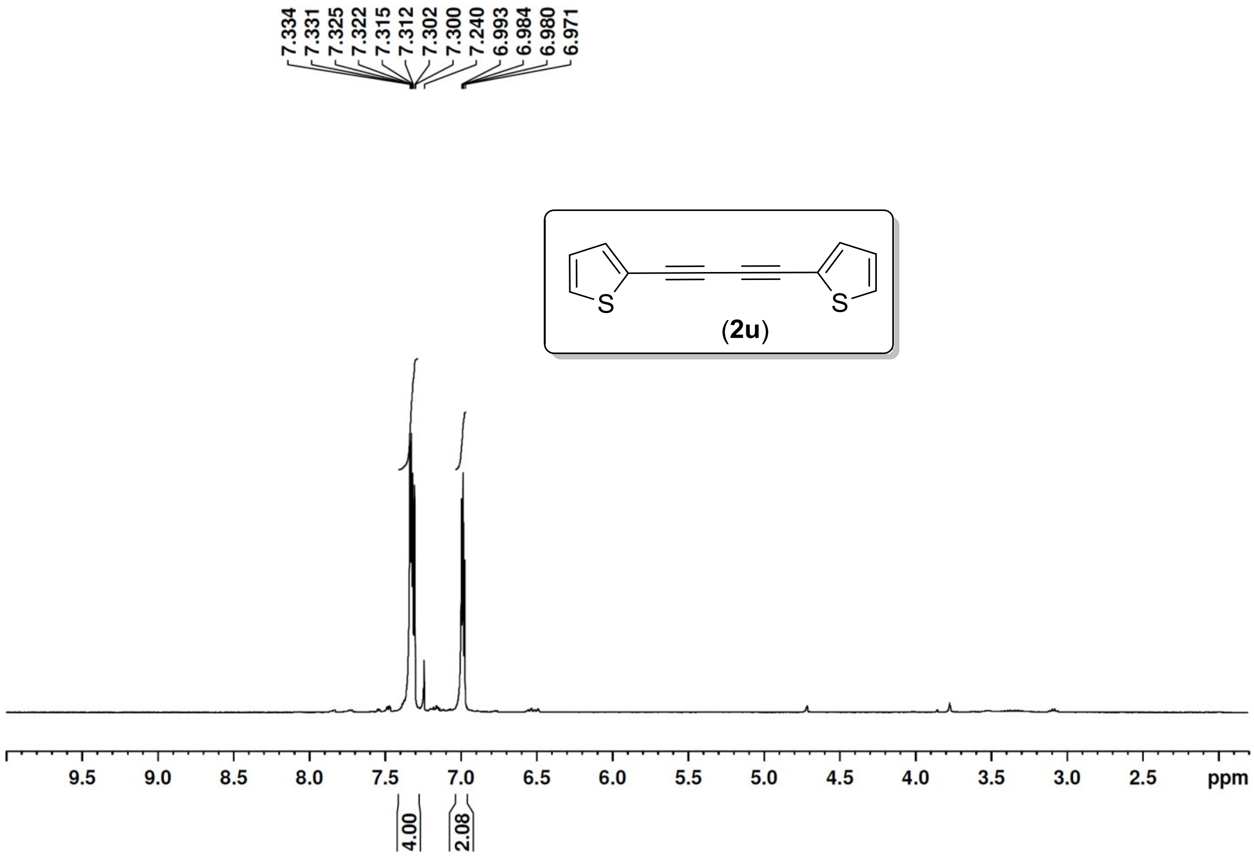

7.976
7.974
7.963
7.961
7.658
7.656
7.645
7.643
7.491
7.489
7.478
7.476
7.466
7.463
7.415
7.412
7.401
7.399
7.389
7.387
7.240
3.946
CO2Me MeO2C
(2r)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
1.11
1.28
1.19
1.11
3.00

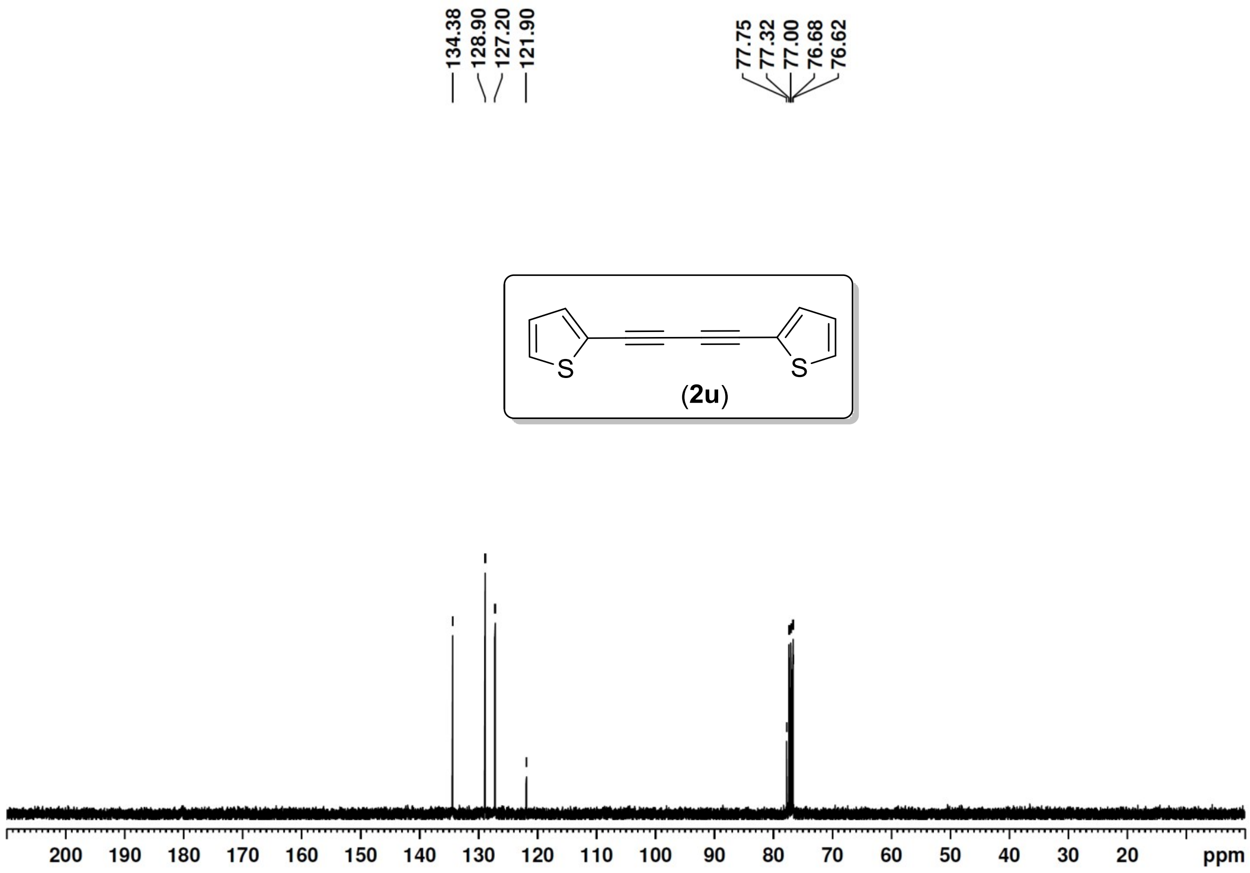

166.11
135.16
132.72
131.80
130.59
128.71
122.55
81.46
78.90
77.21
77.00
76.79
52.33
CO2Me MeO2C
(2r)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

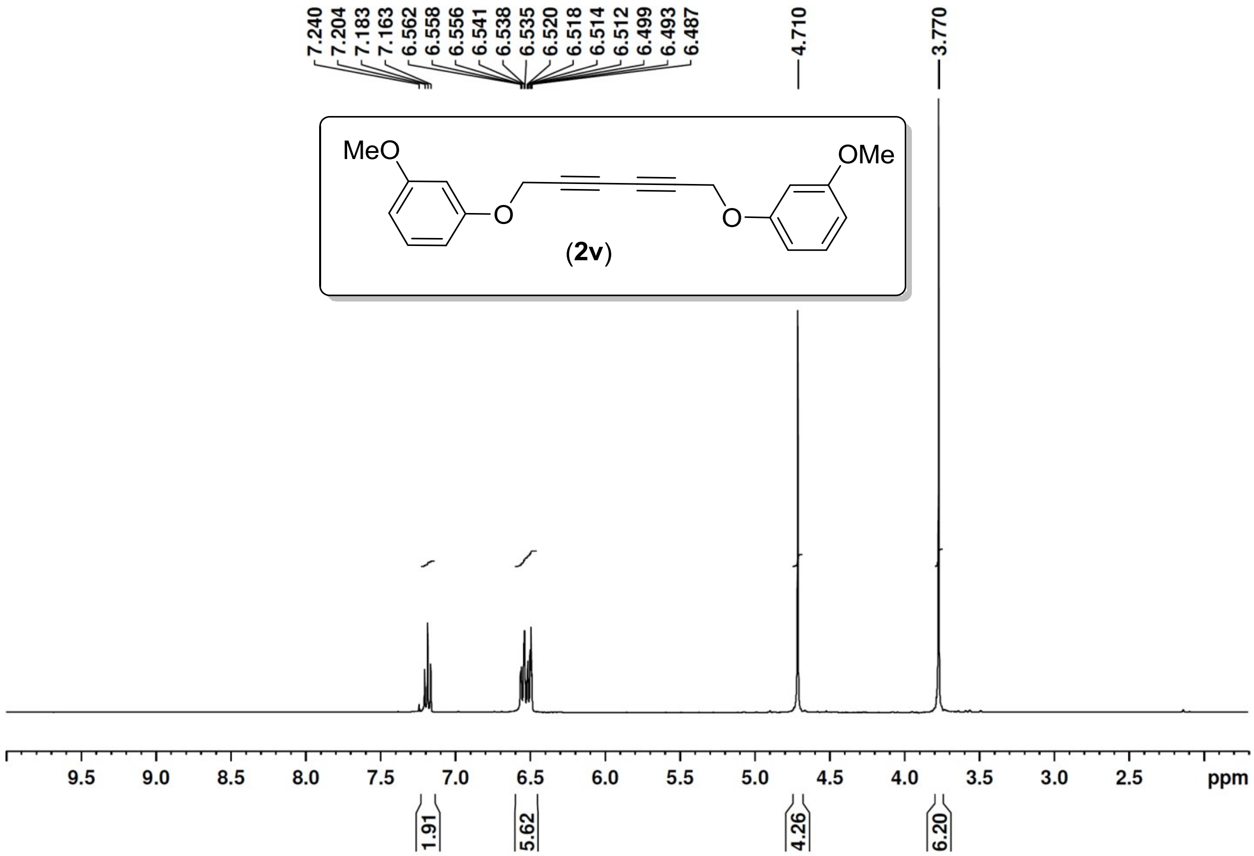

7.954
7.870
7.240
F3C
CF3
F3C
CF3
(2s)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.00
2.09


132.87
132.53
132.44
132.40
132.19
131.85
126.75
124.04
123.59
123.07
123.04
123.00
121.33
118.62
79.68
77.32
77.00
76.68
76.09
F3C
CF3
F3C
CF3
(2s)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

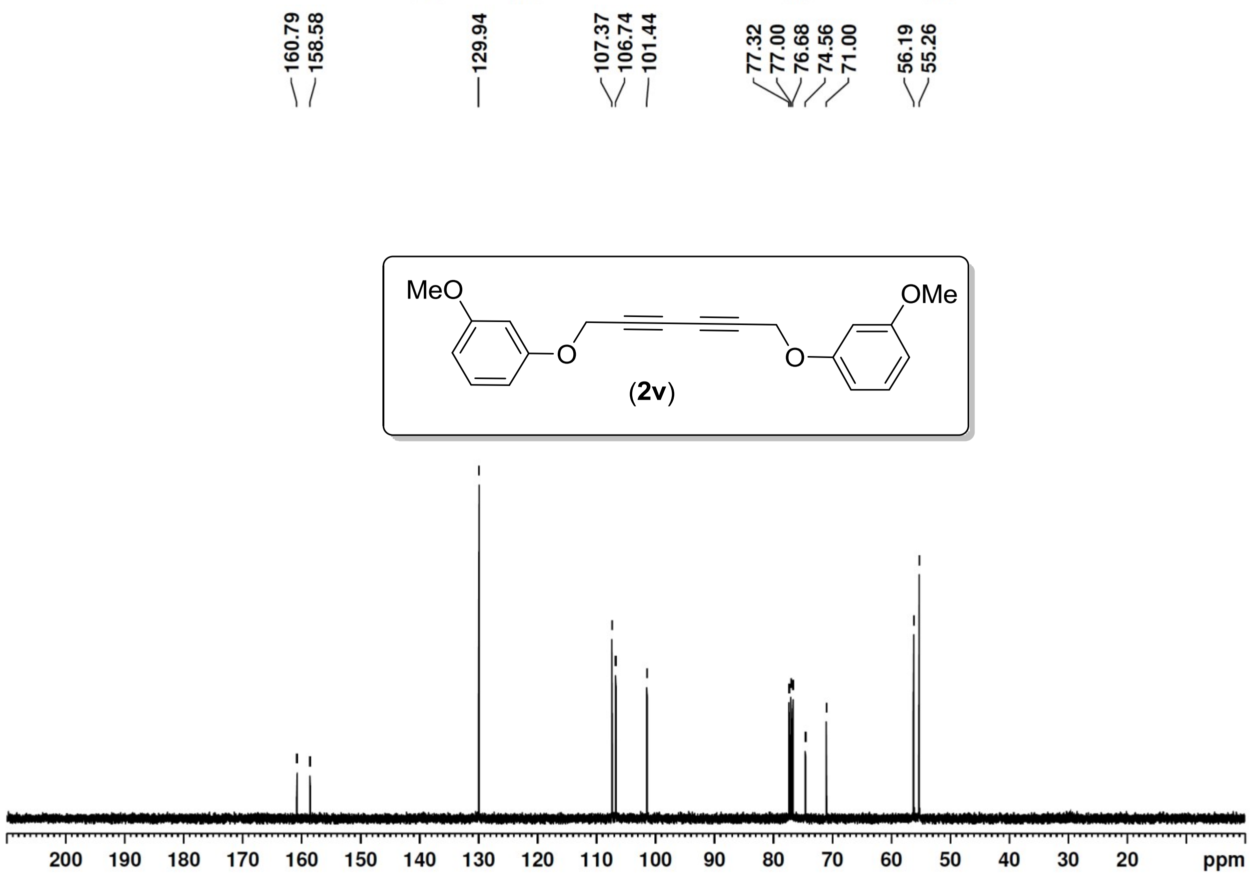

1314 chloro
exp3 stdlh
SAMPLE
date Feb 8 2013
solvent CDCl3
file exp
ACQUISITION
sfrq 400.444
tn H1
at 1.995
np 23964
sw 6006.0
fb 3400
bs 4
tpwr 57
pw 7.0
d1 1.000
tof 0
nt 100
ct 56
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -0.1
wp 4404.8
vs 60
sc 0
wc 250
hzmm 17.62
is 204.98
rfl 3937.4
rfp 2899.2
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.444
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
7.688
7.673
7.657
7.535
7.517
7.516
7.498
7.480
7.461
7.441
7.240
1.251
CF3
F3C
(2t)
10
9
8
7
6
5
4
3
2
1
ppm
27.99

1314 chloro
exp2 stdl3c
SAMPLE
date Feb 8 2013
solvent CD3OD
file exp
ACQUISITION
sfrq 100.701
tn C13
at 1.199
np 59968
sw 25000.0
fb 13800
bs 4
tpwr 58
pw 8.7
d1 0
tof 0
nt 10000
ct 416
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -0.5
wp 22151.9
vs 80
sc 0
wc 250
hzmm 88.61
is 500.00
rfl 10361.5
rfp 7753.2
th 2
ins 100.000
nm no ph
DEC. & VT
dfrq 400.446
dn H1
dpwr 39
dof 0
dm yyy
dmm w
dmf 9000
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
135.116
132.668
132.365
131.501
129.145
126.091
126.046
125.993
125.947
124.599
121.886
119.643
78.690
78.553
77.318
77.000
76.682
29.704
CF3
F3C
(2t)
200
180
160
140
120
100
80
60
40
20
ppm


7.334
7.331
7.325
7.322
7.315
7.312
7.302
7.300
7.240
6.993
6.984
6.980
6.971
S
S
(2u)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
4.00
2.08

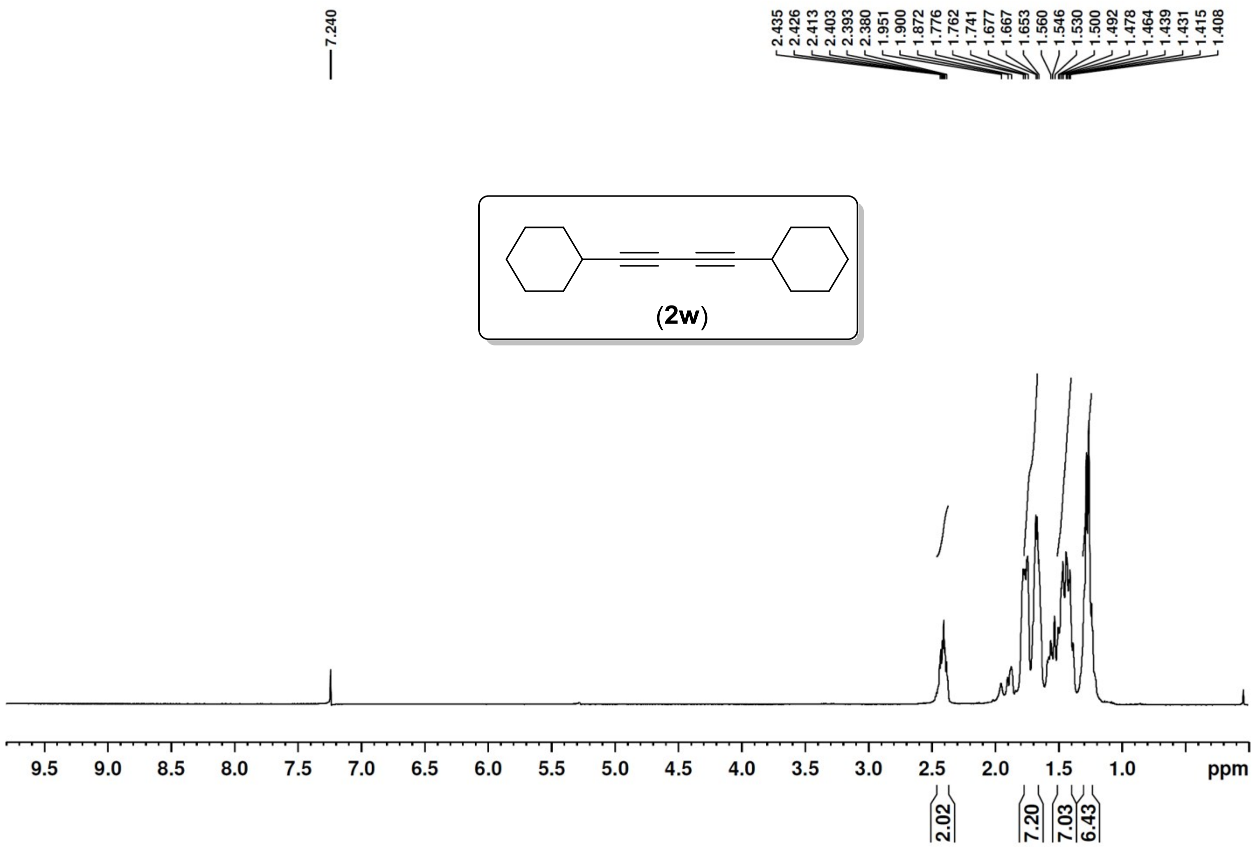

134.38
128.90
127.20
121.90
77.75
77.32
77.00
76.68
76.62
S
S
(2u)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

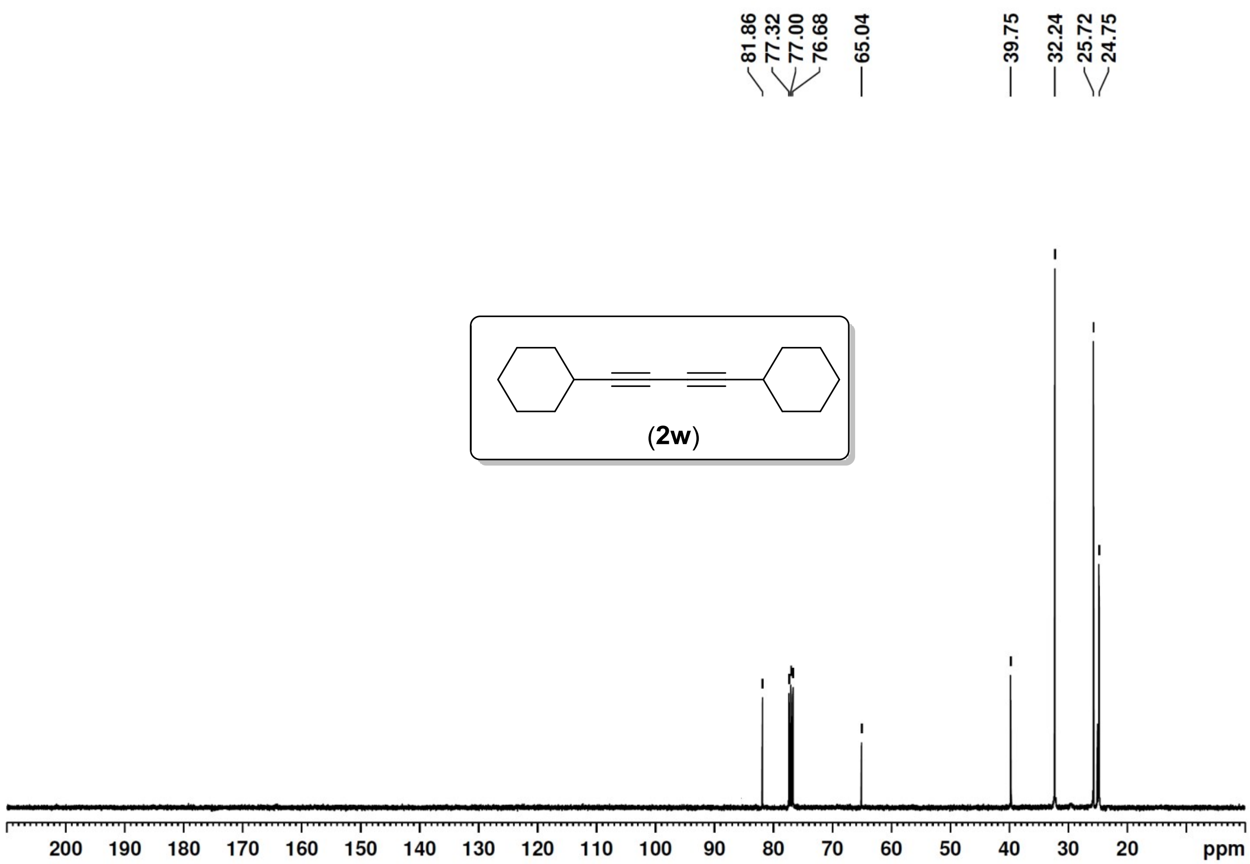


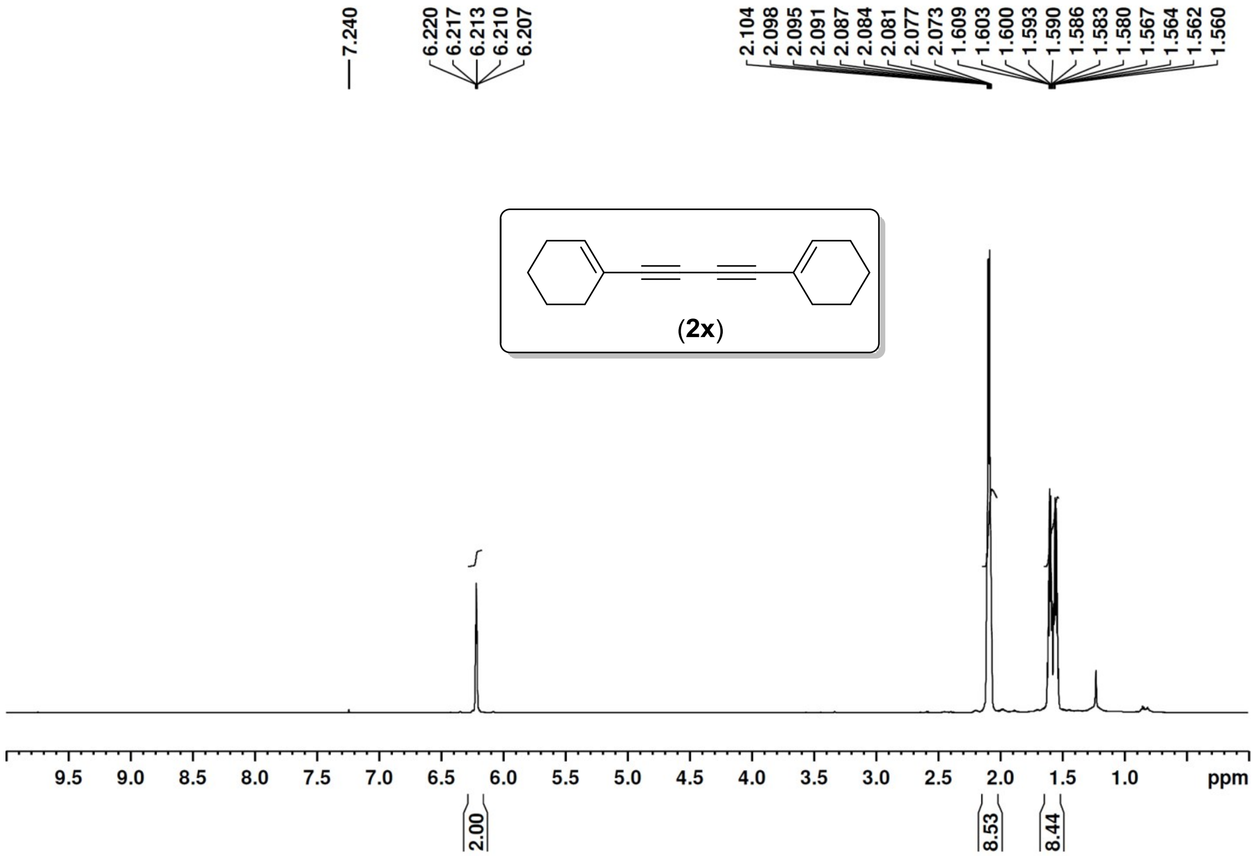
7.240
7.204
7.183
7.163
6.562
6.558
6.556
6.541
6.538
6.535
6.520
6.518
6.514
6.512
6.499
6.493
6.487
4.710
3.770
MeO
OMe
O
O
(2v)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
1.91
5.62
4.26
6.20

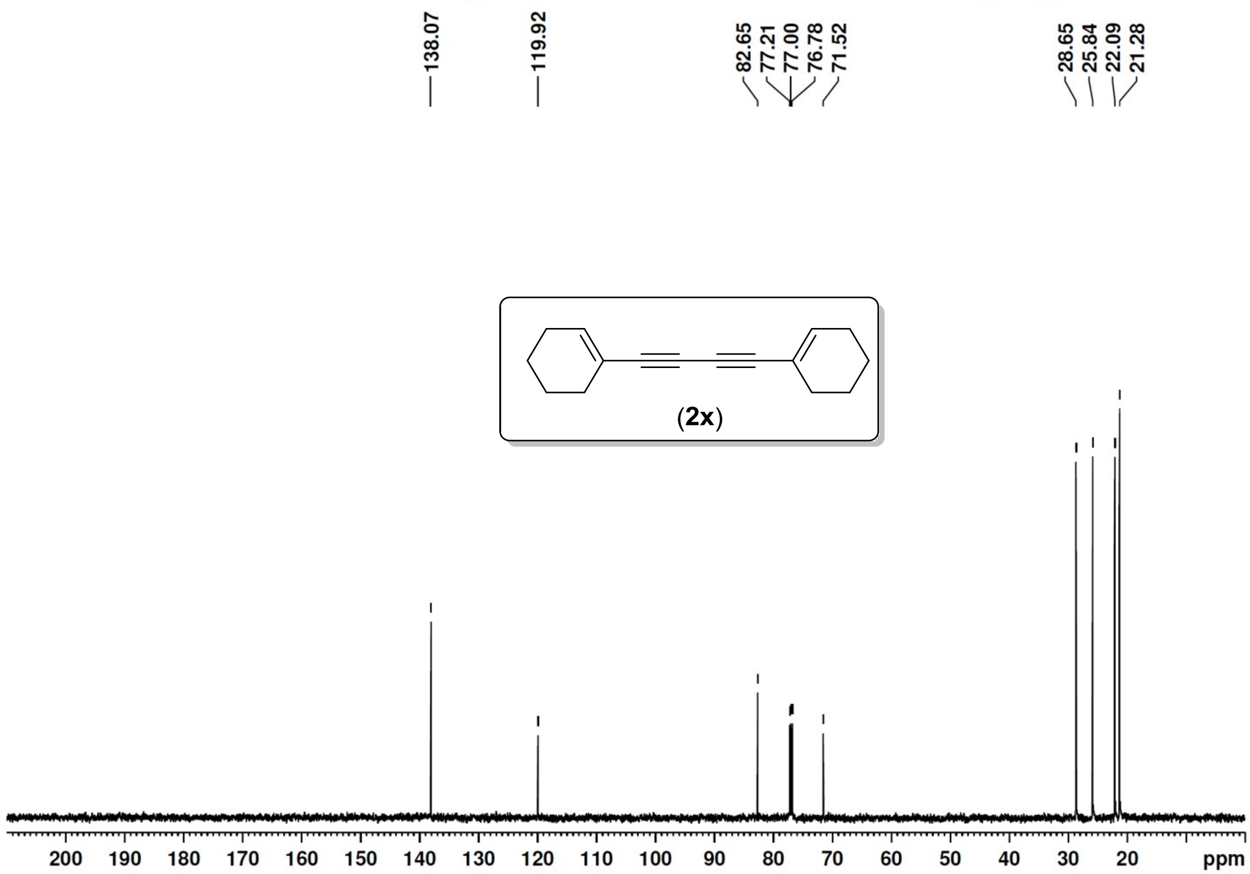


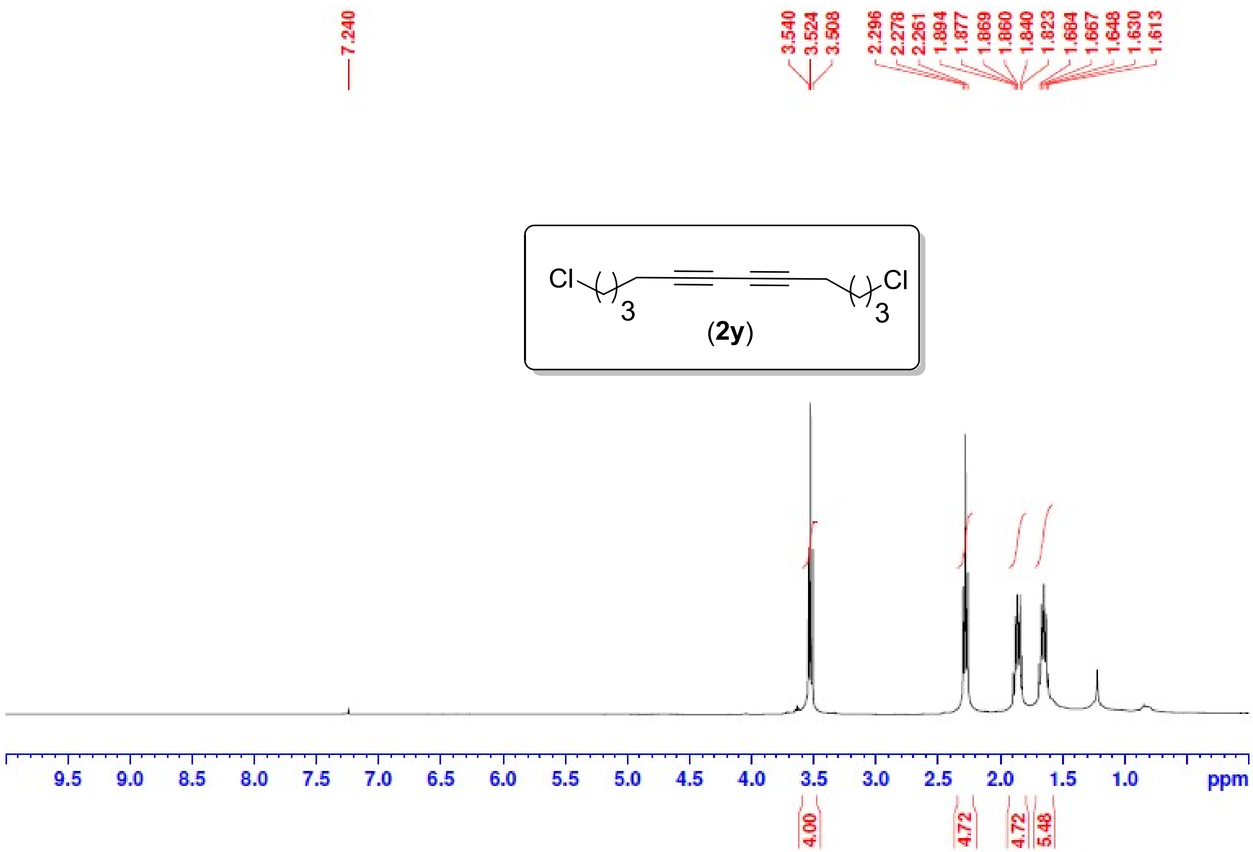
160.79
158.58
129.94
107.37
106.74
101.44
77.32
77.00
76.68
74.56
71.00
56.19
55.26
MeO
OMe
O
O
(2v)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

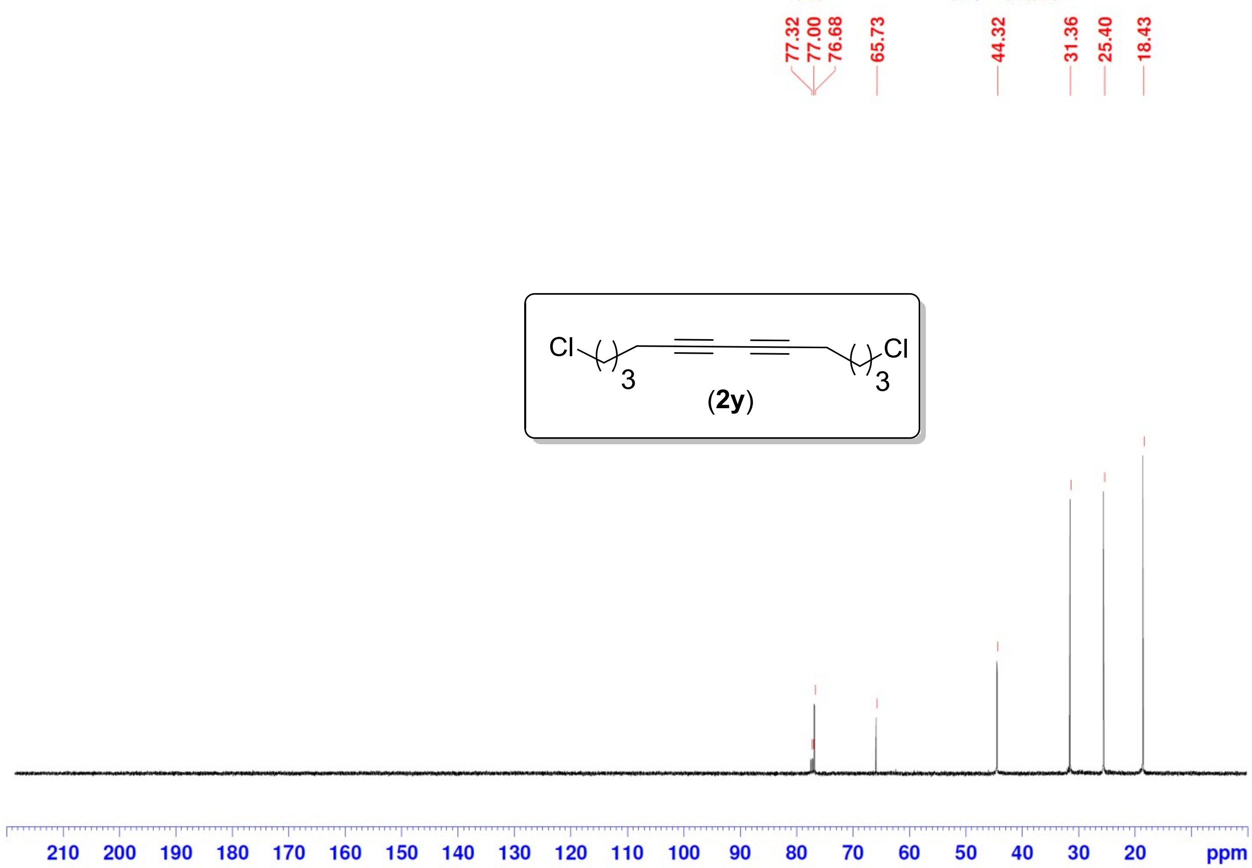

7.240
2.435
2.426
2.413
2.403
2.393
2.380
1.951
1.900
1.872
1.776
1.762
1.741
1.677
1.667
1.653
1.560
1.546
1.530
1.500
1.492
1.478
1.464
1.439
1.431
1.415
1.408
(2w)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.02
7.20
7.03
6.43

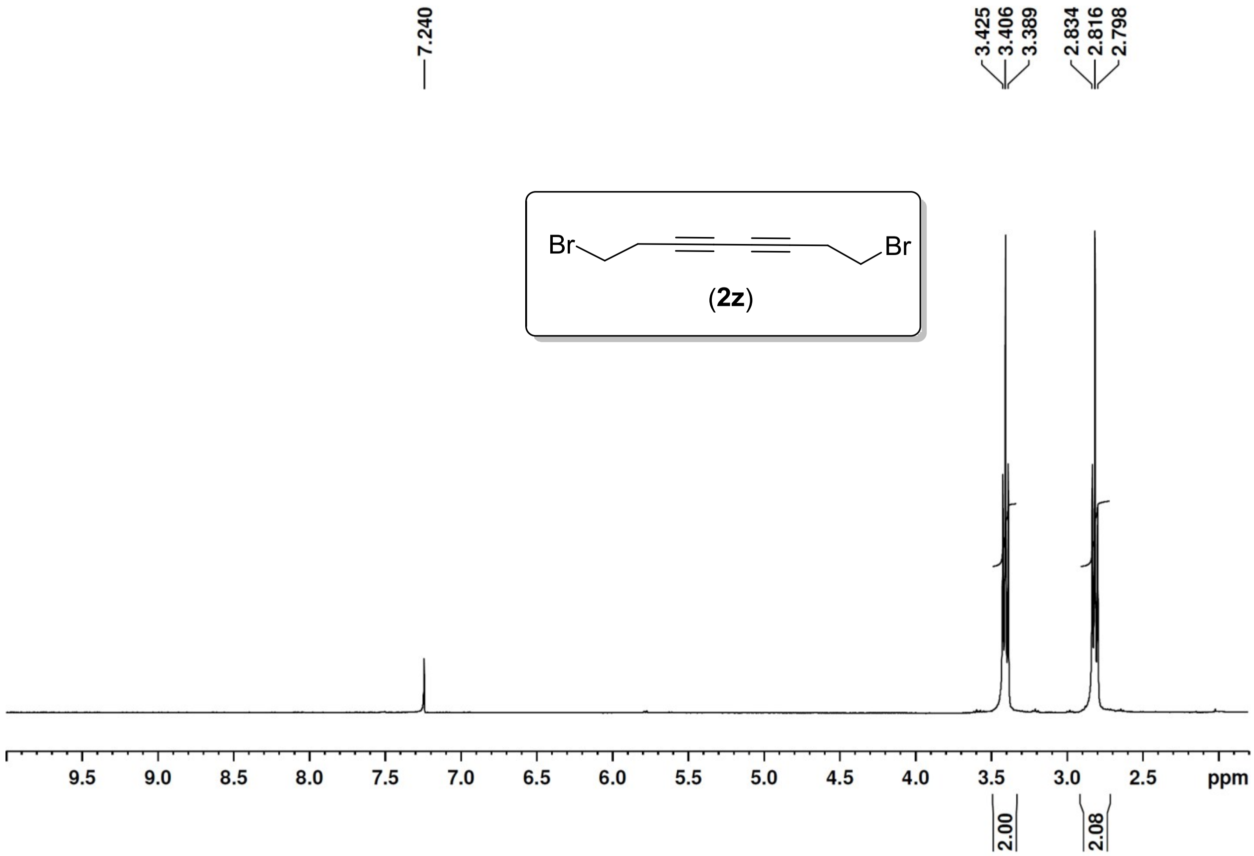

81.86
77.32
77.00
76.68
65.04
39.75
32.24
25.72
24.75
(2w)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

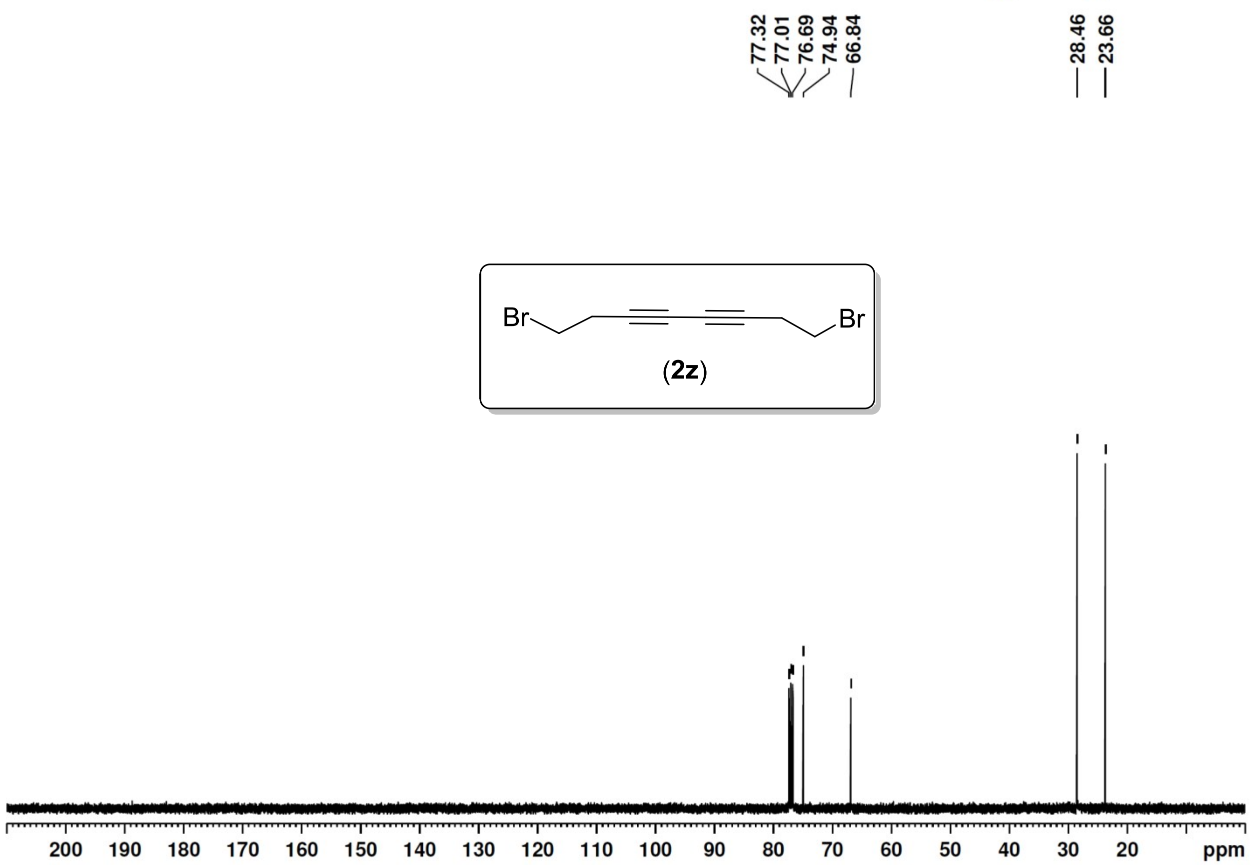

7.240
6.220
6.217
6.213
6.210
6.207
2.104
2.098
2.095
2.091
2.087
2.084
2.081
2.077
2.073
1.609
1.603
1.600
1.593
1.590
1.586
1.583
1.580
1.567
1.564
1.562
1.560
(2x)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
8.53
8.44

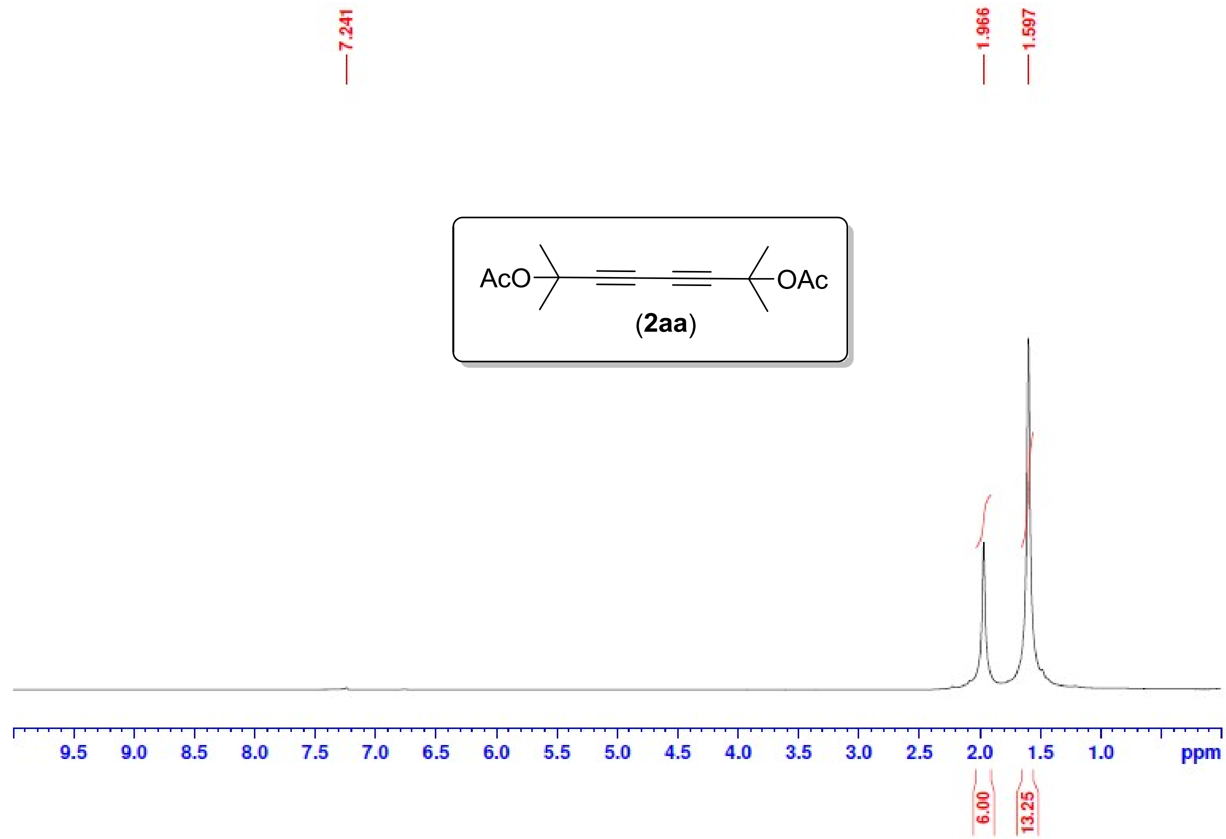

138.07
119.92
82.65
77.21
77.00
76.78
71.52
28.65
25.84
22.09
21.28
(2x)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

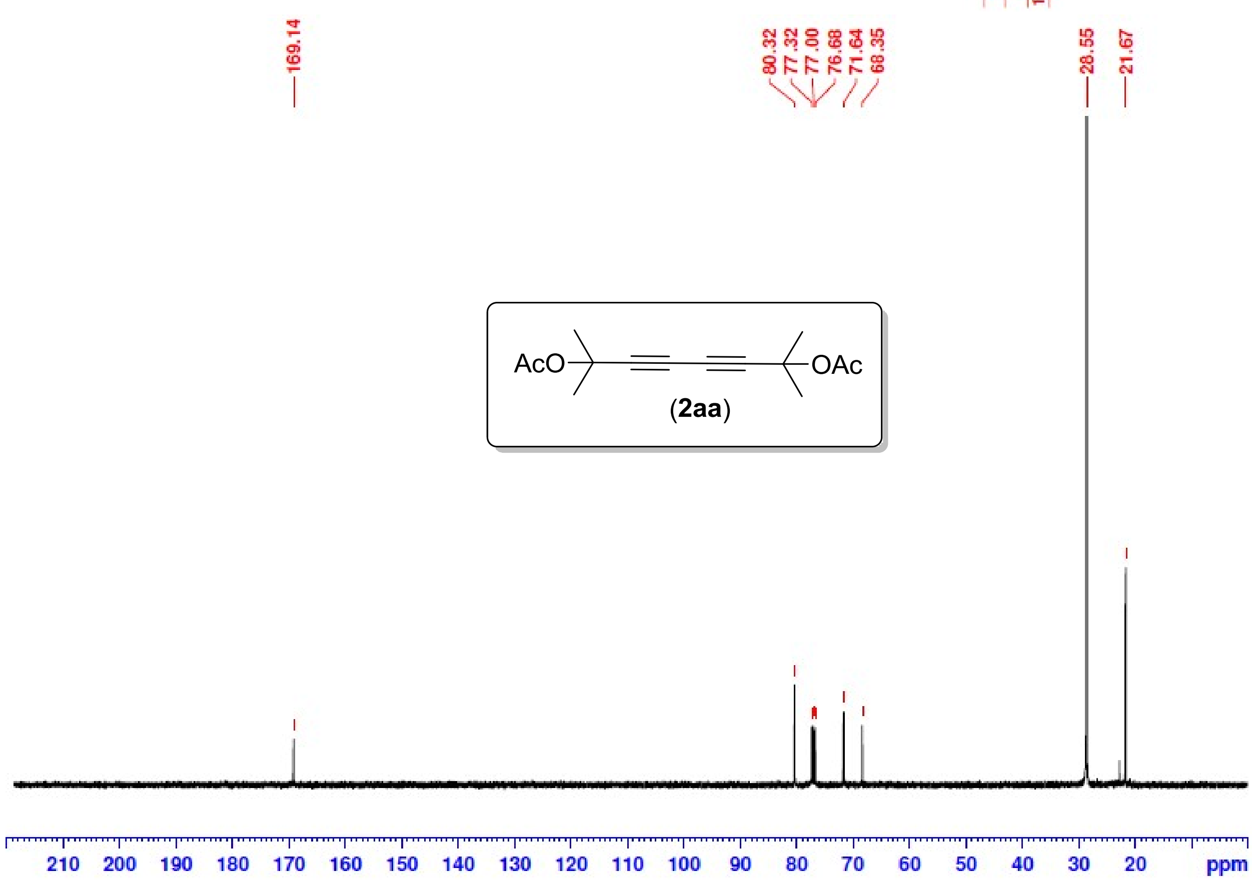

7.240
3.540
3.524
3.508
2.296
2.278
2.261
1.894
1.877
1.869
1.860
1.840
1.823
1.684
1.667
1.648
1.630
1.613
Cl
3
Cl
3
(2y)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.00
4.72
4.72
5.48

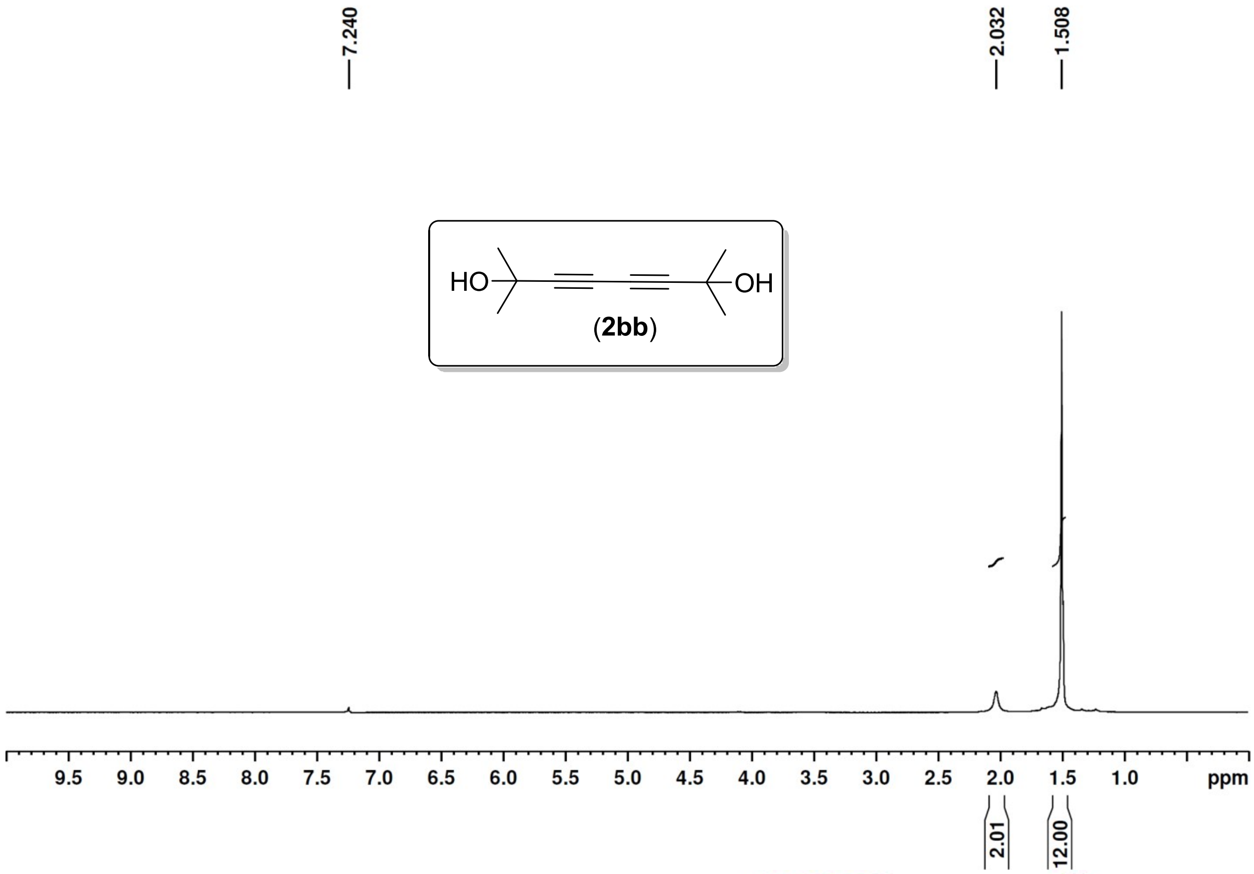

77.32
77.00
76.68
65.73
44.32
31.36
25.40
18.43
Cl
3
Cl
3
(2y)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

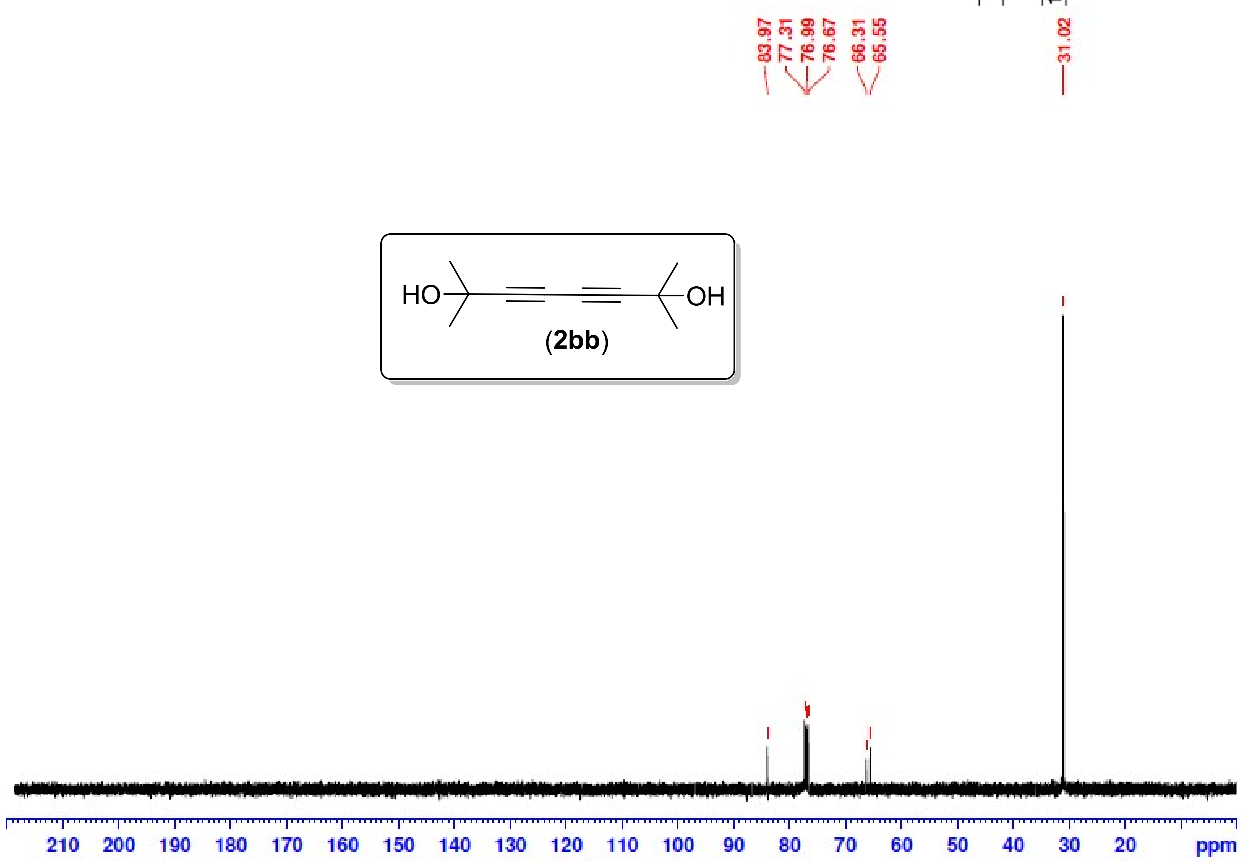

7.240
3.425
3.406
3.389
2.834
2.816
2.798
Br
Br
(2z)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
2.00
2.08

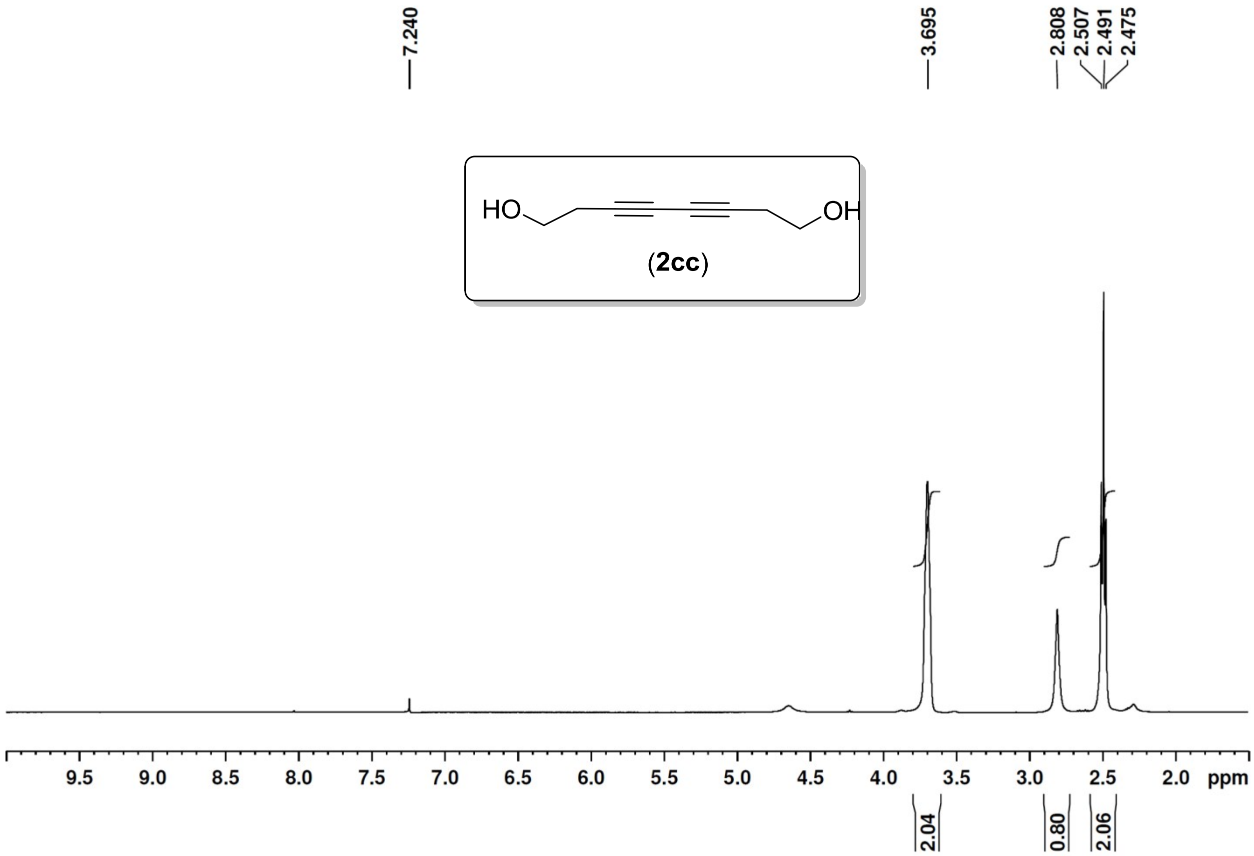

77.32
77.01
76.69
74.94
66.84
28.46
23.66
Br
Br
(2z)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

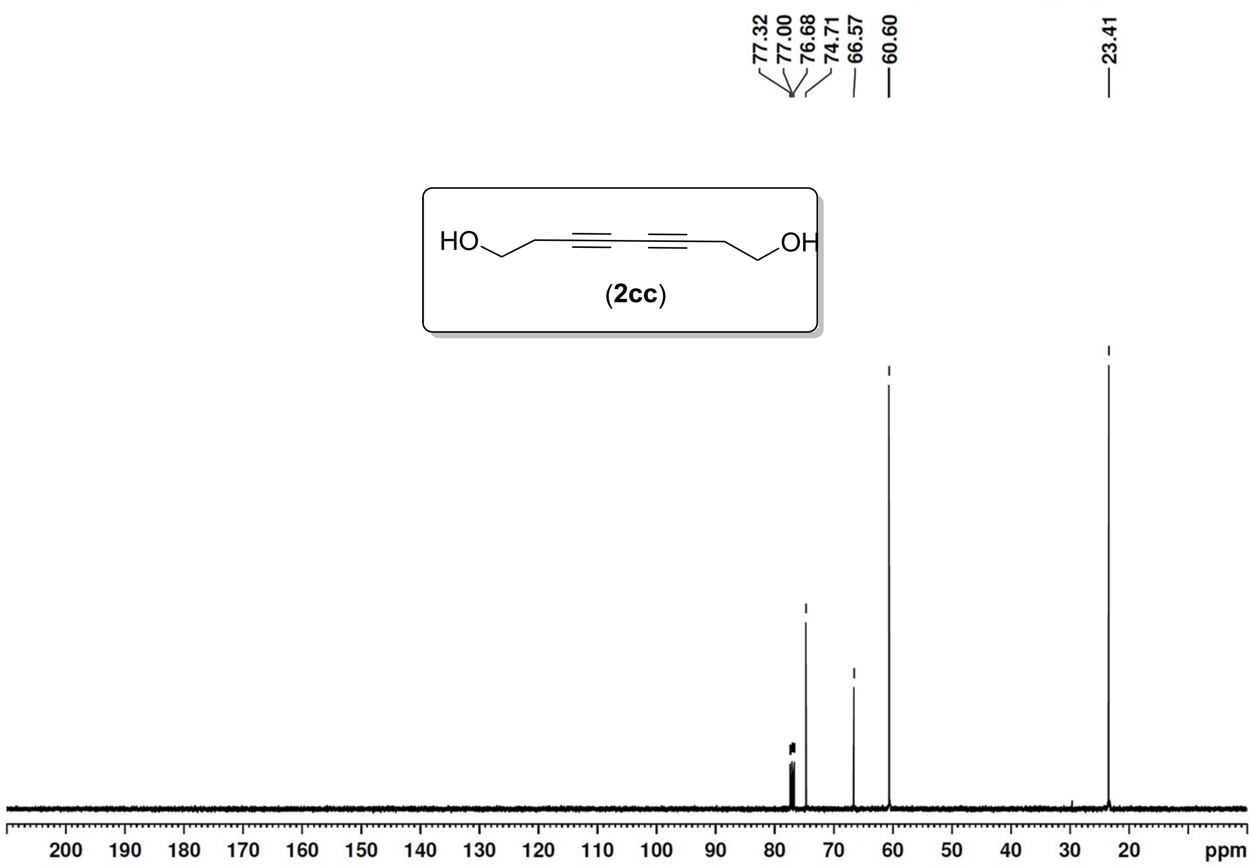

7.241
1.966
1.597
AcO
OAc
(2aa)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
6.00
13.25

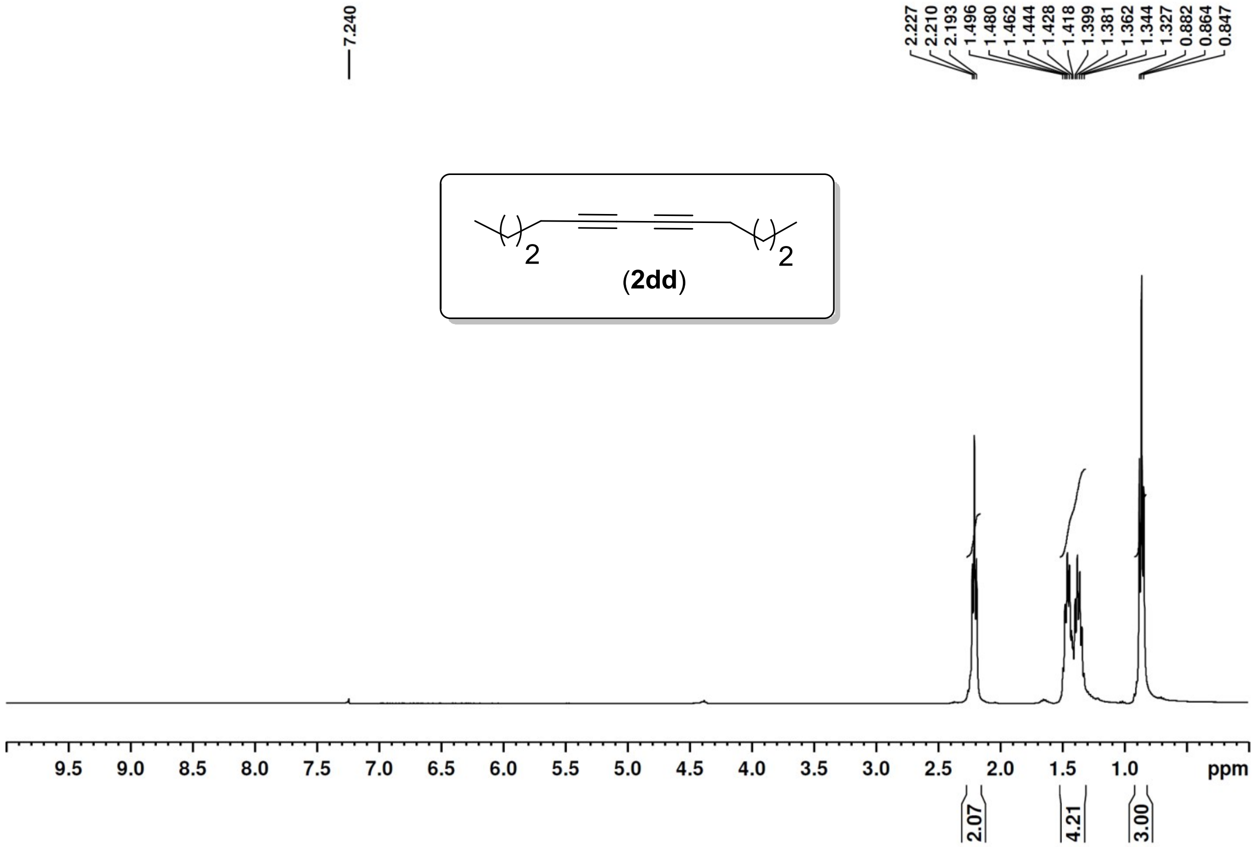

169.14
80.32
77.32
77.00
76.68
71.64
68.35
28.55
21.67
AcO
OAc
(2aa)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

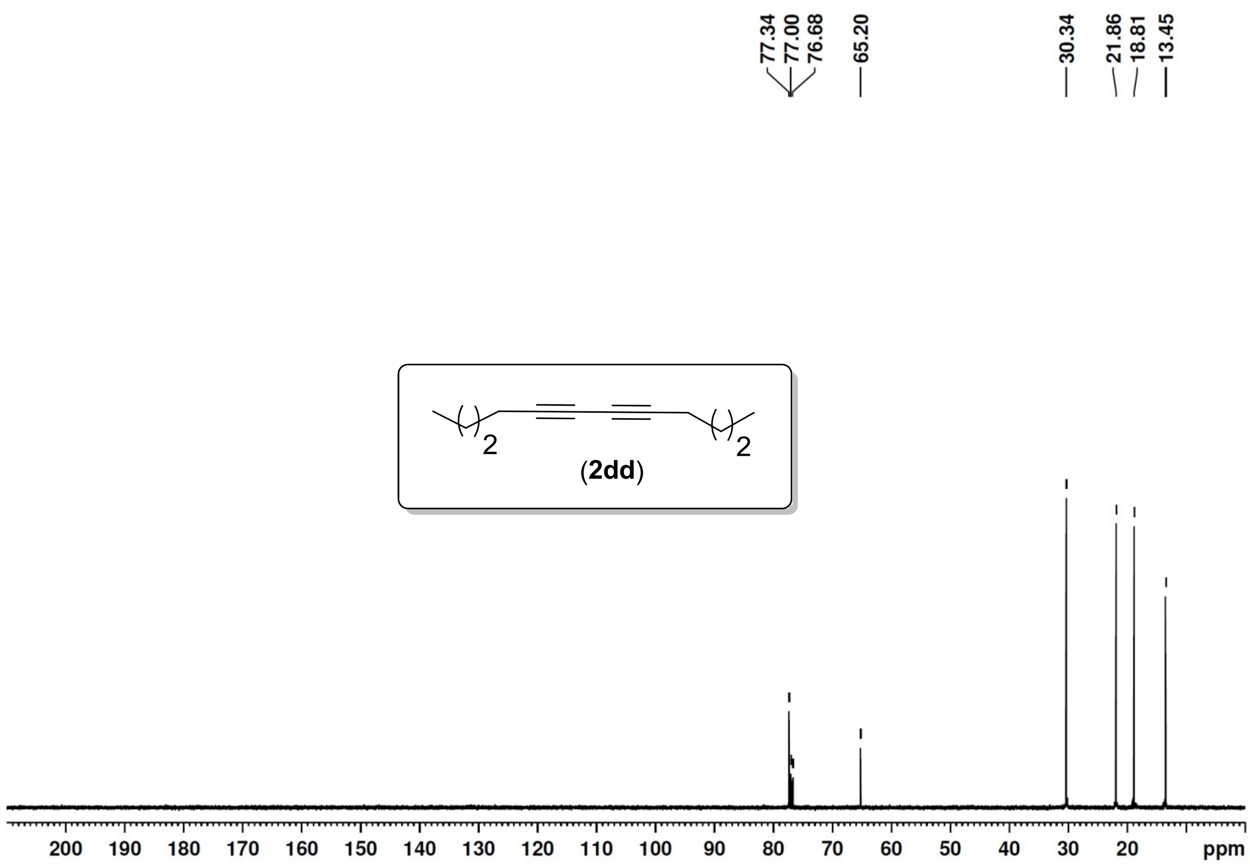

7.240
2.032
1.508
HO
OH
(2bb)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.01
12.00


83.97
77.31
76.99
76.67
66.31
65.55
31.02
HO
OH
(2bb)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.240
3.695
2.808
2.507
2.491
2.475
HO
OH
(2cc)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
2.04
0.80
2.06


77.32
77.00
76.68
74.71
66.57
60.60
23.41
HO
OH
(2cc)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.240
2.227 2.210 2.193 1.496 1.480 1.462 1.444 1.428 1.418 1.399 1.381 1.362 1.344 1.327 0.882 0.864 0.847
(2dd)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.07 4.21 3.00


77.34 77.00 76.68 65.20 30.34 21.86 18.81 13.45
(2dd)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm